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**Eye/Sensor Protection Against Laser Irradiation
Organic Nonlinear Optical Materials**

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EYE/SENSOR PROTECTION AGAINST LASER IRRADIATION ORGANIC NONLINEAR OPTICAL MATERIALS

INTRODUCTION

Lasers are playing an important and increasing role in modern society. Their present uses range from compact disc players to optical data-storage and communication systems. Because of this wide-spread use, the continuing expansion of lasers into other arenas and the low damage thresholds of human eyes and electro-optic sensors ¹⁻³ (Fig. 1), there is increasing concern about eye and sensor protection from laser irradiation. JFS

Coupling these factors with the varied frequencies available using today's high-powered lasers (Table 1 and Fig. 2) makes eye and sensor protection a complex and difficult task. That is, an eye/sensor protection device must be capable of responding to a wide range of wavelengths (from the UV to the IR), able to handle irradiances on the order of mega to gigawatts/cm², the output currently available in common laboratory environments, and be transparent in the absence of an incident laser beam. Such a protection device must also have a response time on the order of picoseconds (10⁻¹² sec) or better to safeguard against pulsed laser irradiation.

The eye/sensor protection devices available today are narrow band filters^{3,4} that can only protect against a limited number of fixed wavelengths; they cannot protect against a frequency agile laser. Research is underway in many different disciplines to develop frequency agile protection devices and one area that appears particularly promising involves the use of organic polymeric nonlinear optical materials. Nonlinear

MAXIMUM PERMISSIBLE EXPOSURE OF EYES

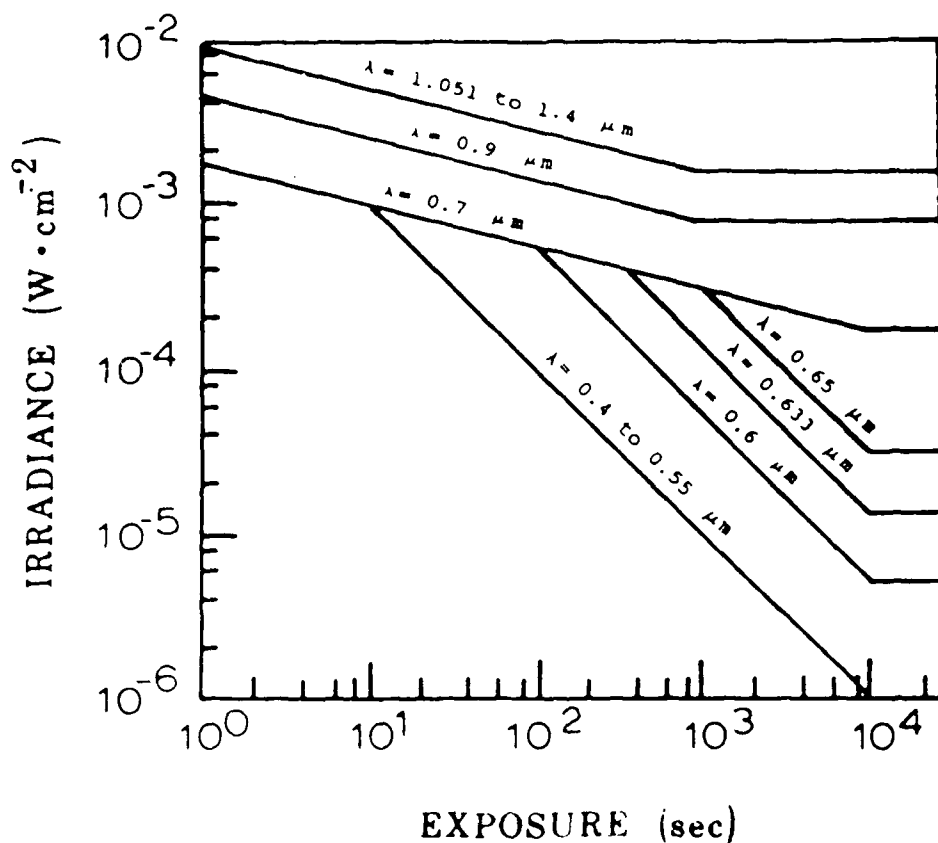


Figure 1: A plot of the maximum exposure of eyes to laser irradiation as a function of irradiance and wavelength. For exposure times greater than 10^4 seconds, there is a constant irradiance threshold. This figure was adapted from Ref. 1.

TABLE 1
LASERS AVAILABLE IN COMMON LABORATORY ENVIRONMENTS

LASER TYPE	OPERATING WAVELENGTH RANGE (micrometers)	OUTPUT POWER	
		CW	PULSED
DYE	0.20 - 0.95		MW
ARGON	0.49, 0.51	Watts	MW
Nd:YAG (2 ω)	0.53		
HeNe	0.63, 0.69	mW	MW
Ti:Sapphire	0.65 - 1.05		MW
RUBY	0.69		MW
Alexandrite	0.70 - 0.82	Watts	MW
GaAs	0.86, 0.91		Watts
Nd:YAG	1.06	Watts	MW
Er:YAG	1.64, 2.8-2.9	Watts	MW
Ho:YAG	2.06		MW
Dy:YAG	2.35		MW
HF	2.6 - 3.0	Watts	MW
DF	3.8 - 4.0		MW
CO	5.0 - 7.0	kW	MW
CO ₂	9.2 - 11.0	kW	MW

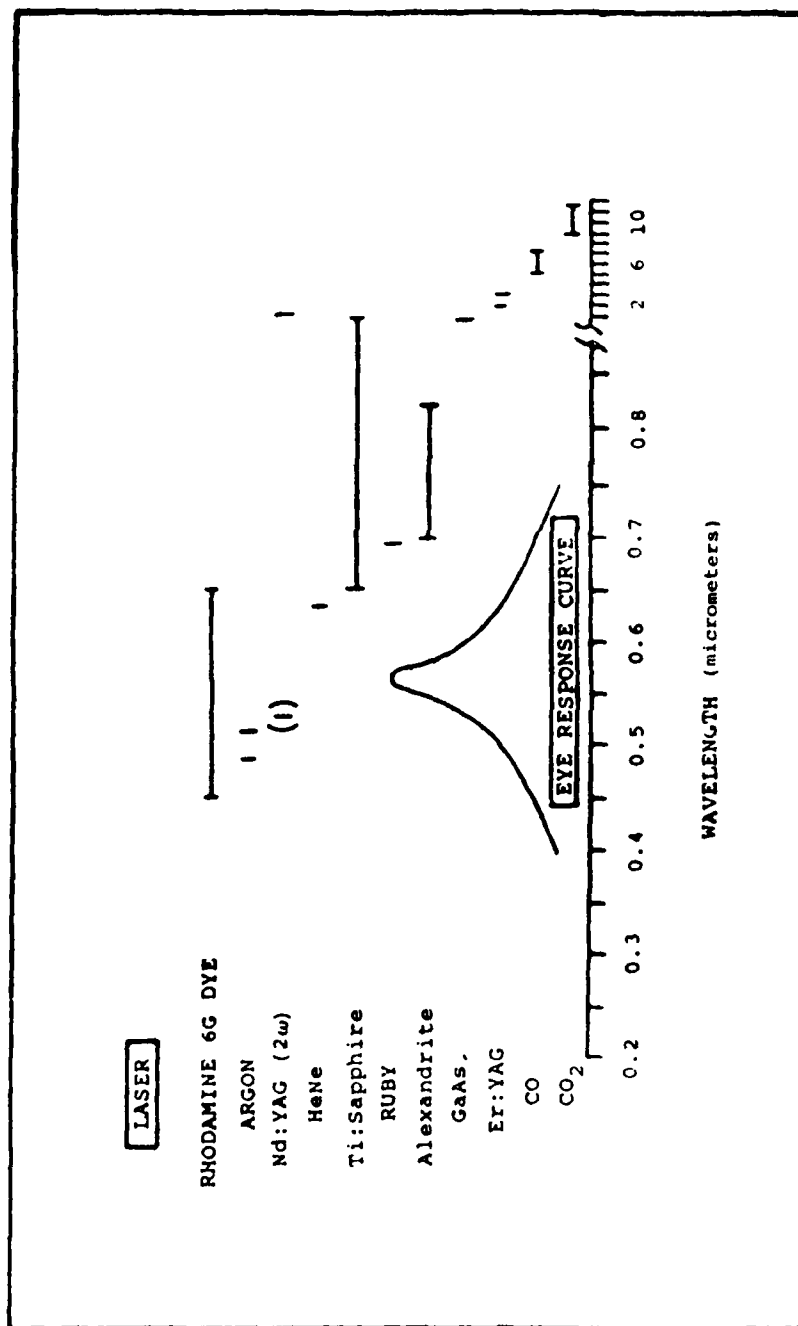


Figure 2: A graphic display of the overlap of lasers commonly available in modern laboratories and the spectral response curve of the human eye; adapted from Ref. 3.

optical materials are those whose optical properties have a nonlinear dependence on the intensity of the incident light. The design flexibility and fast response time (10^{-14} - 10^{-15} sec) offered by organic polymeric nonlinear optical materials has made this a very active and promising research area.^{5-12,15,17-21} (Nonlinear optical processes on this time scale are mainly electronic in nature.⁵⁻¹⁷)

It is the purpose of this report to review the progress that has been made in developing organic polymeric nonlinear optical materials with respect to eye/sensor protection technology. We begin by discussing the functioning of the eye and defining the desired eye protection parameters. This is followed by a brief introduction to the origin of nonlinear optical effects and how they are measured. Recent developments in nonlinear optical organic materials are then presented, with specific examples of proposed or prototyped eye/sensor protection devices following. Finally, future areas of interest are defined.

THE HUMAN EYE

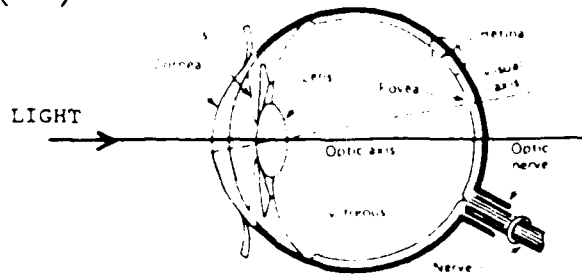
Of all the organs of the human body, the eye is probably the most fascinating and intricate: its sensitivity to brightness can vary by a factor of 100 billion, the dark adapted eye is capable of detecting single photons and it works with nearly 100% quantum efficiency.^{2,22} It is these kinds of extraordinary qualities that make it difficult to protect the eye from laser damage.

VISION

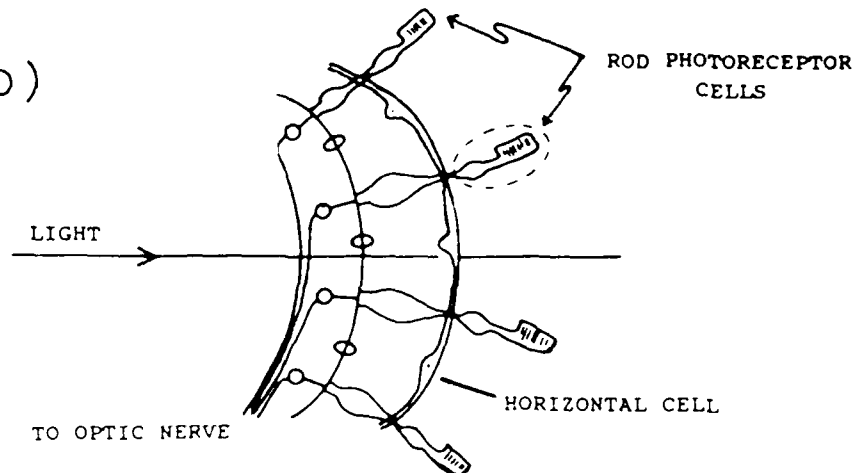
The physical process of vision begins when light enters the eye at the cornea (index of refraction = 1.376)²² which is a major focussing element (Fig. 3a). Further focussing is provided by the lens, the next element in the optical path, which allows for near and distant vision by changing shape. The iris, located behind the lens, is a power limiter; it varies the pupil size, controlling the amount of light entering the eye. The incident light continues on through a clear jelly-like substance, the vitreous humor, onto the photosensitive retina, the detector.

The retina is composed of photoreceptors, nerve cells and pigment layers. The photoreceptors, the light sensitive components, are located in the last cellular layer and point away from the light source (Fig. 3b). There are of two types of photoreceptors, rods and cones. Cones are found packed in the fovea (Fig. 3a) and are responsible for color vision and vision in bright light while the rods are distributed throughout the remainder of the retina and are responsible for vision in dim light.^{2,22} The structure of rods and cones is different (Fig. 3c), the largest difference being in the region

(a)



(b)



(c)

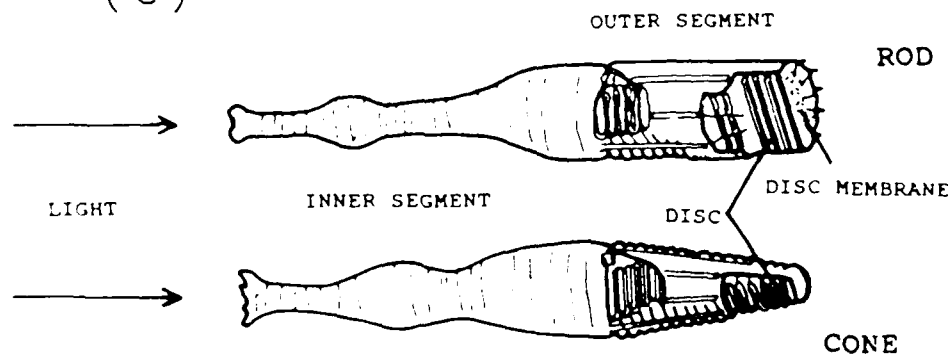


Figure 3: The major components of the human eye are shown in (a), with expanded views of the structure of the retina (b) and of the rod and cone cells (c). This figure was adapted from Ref.22.

where the light absorbing pigments (called rhodopsins) are embedded in regenerating membrane discs.²²

The photosensitive rhodopsins contain the light absorbing molecule retinal which is chemically linked to the protein opsin. The absorption of light induces an isomerization in retinal (Fig. 4) which is thought to cause a structural change in opsin.²² The isomerization of the protein is believed to separate charged groups and thereby effectively store energy (quantum yield of ~60%) within a few picoseconds (10^{-12} secs).²² The transduction of this light-induced response to the neuronal network in the retina is accomplished via the plasma membrane and chemical messengers.²²

VISION DAMAGE

Although vision is limited to the eye's response over a relatively narrow wavelength region (see Fig. 2), light from outside this region can have a profound effect on sight. The cornea absorbs infrared radiation ($1.4-10 \mu\text{m}$)^{1-3,23} and the cornea combined with the lens can absorb near ultraviolet radiation ($0.2-0.4 \mu\text{m}$).^{1-3,23} Therefore, ultraviolet and infrared radiation can damage the cornea causing photokeratitis, corneal burns and cataracts^{1-3,23} and thereby impair vision. However, the greatest danger comes from visible to near-infrared radiation ($0.4 - 1.4 \mu\text{m}$) which the cornea and lens transmit, focussing onto the retina (optical gains on the order of 10^5).¹⁻³ Damage to the part of the retina providing fine detail discrimination and color sensitivity, the fovea, drastically affects vision while damage to the retina outside the fovea does not seriously impair the ability to see.^{2,3} Unfortunately, little recovery is possible from damage to either part of the retina.^{2,3}

Injuries to the eye from laser irradiation are usually grouped into three classes: photochemical, thermal and mechanical.^{1,2,23,24} Photochemical damage involves chemical bond breaking and is associated with long exposures to short wavelength light (blue to ultraviolet).^{2,24} Thermal damage is caused by visible and infrared radiation for pulse lengths of 1 microsecond or longer^{2,24} and includes denaturization processes, i.e., the uncoiling of protein molecules resulting from the breaking of weak hydrogen bonds. Such processes can lead to the rupture of cell walls and enzyme inactivations. Very short pulse lengths (less than microseconds) result in mechanical damage to the eye in the form of acoustic and shock waves.^{2,24} It is the latter two damage mechanisms which are of the greatest interest with respect to eye protection from laser irradiation.

Thermal eye damage is usually discussed in terms of the amount of energy incident on the eye: it is the cumulative energy that causes injury.¹⁻³ The following are commonly used

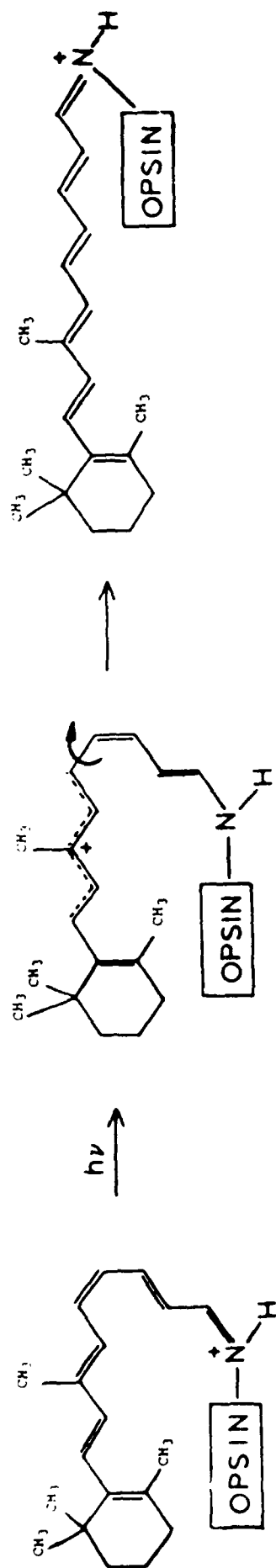


Figure 4: The light induced transformation of cis-retinal to trans-retinal which is believed to cause a conformation change in the protein opsin, beginning the light detection process in human eyes.

EYE DAMAGE VS SPECTRAL REGION

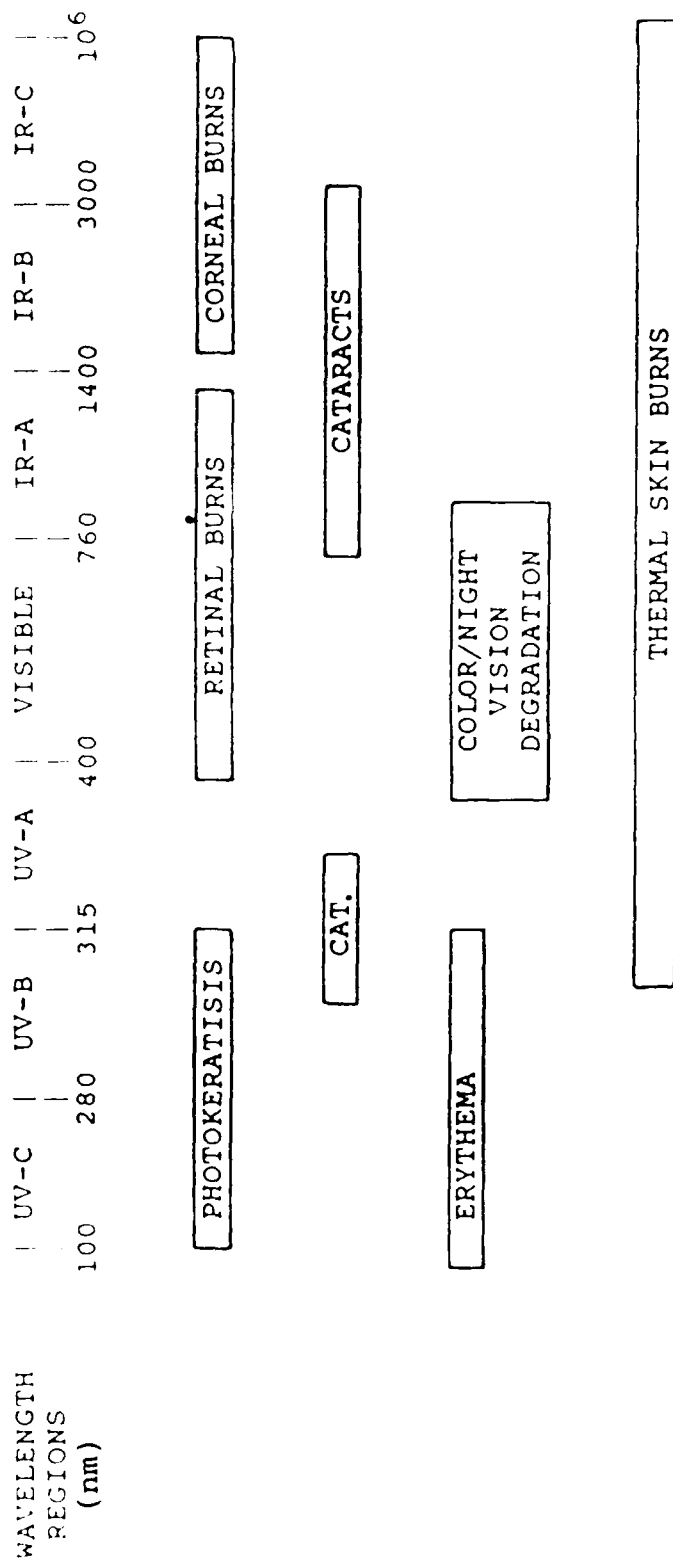


Figure 5: A schematic diagram of the various types of eye and skin damage that can accompany laser irradiation in various wavelength regions; adapted from Ref. 1.

TABLE 2

EYE EXPOSURE LIMITS TO LASER IRRADIATION

Wavelength, λ (μm)	Exposure Duration t (s)	Maximum Permissible Exposure (MPE)	Notes
Ultraviolet			
0.200 to 0.302	10^{-9} to 3×10^4	$3 \times 10^{-3} \text{ J} \cdot \text{cm}^{-2}$	
0.303	10^{-9} to 3×10^4	$4 \times 10^{-3} \text{ J} \cdot \text{cm}^{-2}$	
0.304	10^{-9} to 3×10^4	$6 \times 10^{-3} \text{ J} \cdot \text{cm}^{-2}$	
0.305	10^{-9} to 3×10^4	$1.0 \times 10^{-2} \text{ J} \cdot \text{cm}^{-2}$	
0.306	10^{-9} to 3×10^4	$1.6 \times 10^{-2} \text{ J} \cdot \text{cm}^{-2}$	
0.307	10^{-9} to 3×10^4	$2.5 \times 10^{-2} \text{ J} \cdot \text{cm}^{-2}$	
0.308	10^{-9} to 3×10^4	$4.0 \times 10^{-2} \text{ J} \cdot \text{cm}^{-2}$	
0.309	10^{-9} to 3×10^4	$6.3 \times 10^{-2} \text{ J} \cdot \text{cm}^{-2}$	
0.310	10^{-9} to 3×10^4	$1.0 \times 10^{-1} \text{ J} \cdot \text{cm}^{-2}$	
0.311	10^{-9} to 3×10^4	$1.6 \times 10^{-1} \text{ J} \cdot \text{cm}^{-2}$	
0.312	10^{-9} to 3×10^4	$2.5 \times 10^{-1} \text{ J} \cdot \text{cm}^{-2}$	
0.313	10^{-9} to 3×10^4	$4.0 \times 10^{-1} \text{ J} \cdot \text{cm}^{-2}$	
0.314	10^{-9} to 3×10^4	$6.3 \times 10^{-1} \text{ J} \cdot \text{cm}^{-2}$	
0.315 to 0.400	10^{-9} to 10	$0.56 t^{1/4} \text{ J} \cdot \text{cm}^{-2}$	
0.315 to 0.400	10 to 3×10^4	1 $\text{J} \cdot \text{cm}^{-2}$	or $0.56 t^{1/4} \text{ J} \cdot \text{cm}^{-2}$, whichever is lower.
Visible and Near Infrared			
0.400 to 0.700	10^{-9} to 1.8×10^{-5}	$5 \times 10^{-7} \text{ J} \cdot \text{cm}^{-2}$	
0.400 to 0.700	1.8×10^{-5} to 10	$1.8 t^{3/4} \times 10^{-3} \text{ J} \cdot \text{cm}^{-2}$	
0.400 to 0.550	10 to 10^4	$10 \times 10^{-3} \text{ J} \cdot \text{cm}^{-2}$	
0.550 to 0.700	10 to T_1	$1.8 t^{3/4} \times 10^{-3} \text{ J} \cdot \text{cm}^{-2}$	
0.550 to 0.700	T_1 to 10^4	$10 C_B \times 10^{-3} \text{ J} \cdot \text{cm}^{-2}$	
0.400 to 0.700	10^4 to 3×10^4	$C_B \times 10^{-6} \text{ W} \cdot \text{cm}^{-2}$	
0.700 to 1.050	10^{-9} to 1.8×10^{-5}	$5 C_A \times 10^{-7} \text{ J} \cdot \text{cm}^{-2}$	
0.700 to 1.050	1.8×10^{-5} to 10^3	$1.8 C_A t^{3/4} \times 10^{-3} \text{ J} \cdot \text{cm}^{-2}$	
1.051 to 1.400	10^{-9} to 5×10^{-5}	$5 \times 10^{-6} \text{ J} \cdot \text{cm}^{-2}$	
1.051 to 1.400	5×10^{-5} to 10^3	$9 t^{3/4} \times 10^{-3} \text{ J} \cdot \text{cm}^{-2}$	
0.700 to 1.400	10^3 to 3×10^4	$320 C_A \times 10^{-6} \text{ W} \cdot \text{cm}^{-2}$	
Far Infrared			
1.4 to 10^3	10^{-9} to 10^{-7}	$10^{-2} \text{ J} \cdot \text{cm}^{-2}$	
	10^{-7} to 10	$0.56 t^{1/4} \text{ J} \cdot \text{cm}^{-2}$	
	>10	0.1 $\text{W} \cdot \text{cm}^{-2}$	
1.54 only	10^{-9} to 10^{-6}	1.0 $\text{J} \cdot \text{cm}^{-2}$	

$C_A = 1$ for $\lambda = 0.400$ to $0.700 \mu\text{m}$,
 $C_A = 10^{2.00 - 0.700\lambda}$ for $\lambda = 0.700$ to $1.050 \mu\text{m}$,
 $C_A = 5$ for $\lambda = 1.050$ to $1.400 \mu\text{m}$,
 $C_B = 1$ for $\lambda = 0.400$ to $0.550 \mu\text{m}$,
 $C_B = 10^{1.50 - 0.550\lambda}$ for $\lambda = 0.550$ to $0.700 \mu\text{m}$,
 $T_1 = 10 \times 10^{2.00 - 0.550\lambda}$ for $\lambda = 0.550$ to $0.700 \mu\text{m}$.

*Adapted from Ref. 1

eye damage thresholds, W_e :¹

* For pulse durations of 1 - 18 ns: $W_e = 0.5 \mu\text{J}/\text{cm}^2$

* For longer pulse durations, up to 10 s: s:

$$W_e = 1.8 t^{3/4} \text{ mJ}/\text{cm}^2 \quad (t \text{ in seconds})$$

As an example, using the forementioned damage thresholds and a value of $100 \text{ mW}/\text{cm}^2$ for the output of the sun,² an eye protection device must attenuate the light by a factor equivalent to 1.5 optical density units (ODU) (a transmission reduction of 97%) when directed at the sun.

PROTECTION STRATEGIES

Any successful eye/sensor protection device must interact with and attenuate the laser light before it reaches the detector system. The interaction of light with matter is usually classified in one of three categories: absorption, dispersion or scattering. Absorption can be an effective protection strategy and representative examples of absorption devices under investigation include particle suspension, chalcogenide, VO_2 , Ge, and two-photon absorption activated power limiters. However, such devices often have reduced transparency in the visible spectral region or unacceptable response times. Therefore, much of the recent research into eye/sensor protection has focussed on using dispersion or scattering to redirect the light and this is where nonlinear optical materials have the greatest potential for impact in the near term: nonlinear optical materials can have unique index of refraction properties and fast response times.

ORGANIC NONLINEAR OPTICAL MATERIALS

Nonlinear optical materials have been known and studied for over two decades with most research efforts being successfully directed at inorganic materials,^{5,25,26} in particular, inorganic crystals²⁷, glasses^{28,29} and semiconductors.³⁰⁻³² The most familiar example of inorganic nonlinear optical materials are crystals such as potassium dihydrogen phosphate (KDP) and lithium niobate (LiNbO_3). However, more recently, interest has focussed on such inorganic materials as tungsten bronze crystals.³³ With the recent emphasis on optical computing and communication, a need for nonlinear optical materials with better mechanical processing and physical properties than available in typical inorganic nonlinear optical materials has become apparent and researchers have turned to examine organic polymeric materials.^{9,14,17-21,34-39} It is now generally agreed that organic materials have the potential for nonlinear optical effects which are orders of magnitude better than currently used inorganic materials.^{5,6,12,14,17-21,34,37,38,40-45} This is based on the origin of the nonlinear optical effect in organic materials: the easily polarized molecular electric fields.^{7,10,14,15} Extensive research is underway on the development of nonlinear optical organic materials and a

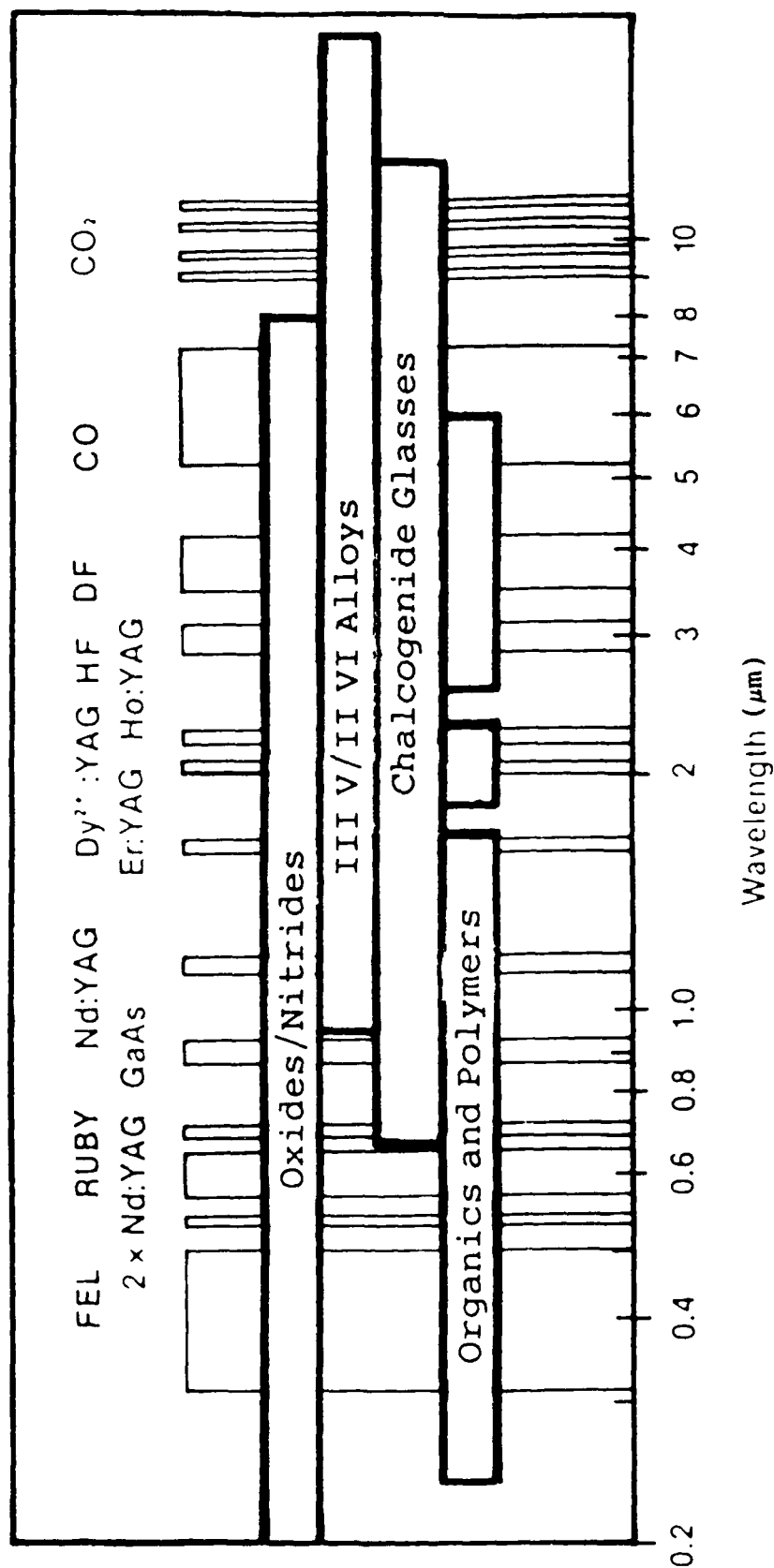


Figure 6: A graphic representation of various lasers available in modern laboratories and the spectral transmission windows of potential laser hardening materials.

detailed theoretical understanding and description of the origin of these optical effects.^{5-21, 26-189} It is the latter that is discussed in the following section.

THEORY

Linear Refractive Index

In order to develop a more comprehensive understanding of nonlinear optical effects and materials, it will be useful to briefly examine the origin of the linear refractive index.

Consider the classical model (Lorentzian) of an atom with one electron and the effect of applying a static electric field: the electron-nucleus distance is altered - a polarization is induced. For the simple case considered here, the distance change is linearly proportional to the applied field. If an oscillating electric field (like in a low intensity monochromatic light beam) is applied, the electron oscillates about its equilibrium position. This oscillating dipole emits electromagnetic radiation (light) at the same frequency as the incident light but with a different phase due to the restoring forces acting on the electron.

Extending this simple example to include a row of N atoms (Fig. 7), we see that a monochromatic light wave having passed through the N atoms will have a different phase than if it had not. That is, the light wave appears to move more slowly through the sample than through the surrounding vacuum. The phase difference is directly related to the number of atoms in the row, N , and therefore to the sample length or thickness. The ratio of the speed of light in the sample, C_{sample} , and in vacuum, C_{vacuum} , is known as the index of refraction, $n = C_{\text{vacuum}}/C_{\text{sample}}$.

An oscillating dipole has a toroidal shaped radiation pattern (a $\sin \theta$ dependence, where θ is the angle between the axis of the dipole and the direction of observation) and therefore reradiates light in many directions. However, only the reradiation in the forward direction is phase-matched and therefore additive. That is, any radiation not in the forward direction is out of phase with the radiation in that same direction from other atoms and so destructively interferes. Also implicit in the simple models discussed above, is that all the dipoles radiate the same fraction of the incident wave. If one group of dipoles radiates a different fraction, some of the reradiated light will be visible in other directions - scattered radiation.

Molecular Polarizability

Noncentrosymmetric molecules (those without a center of symmetry) have complex charge distributions and, therefore, possess an intrinsic dipole. Placing such a molecule in a

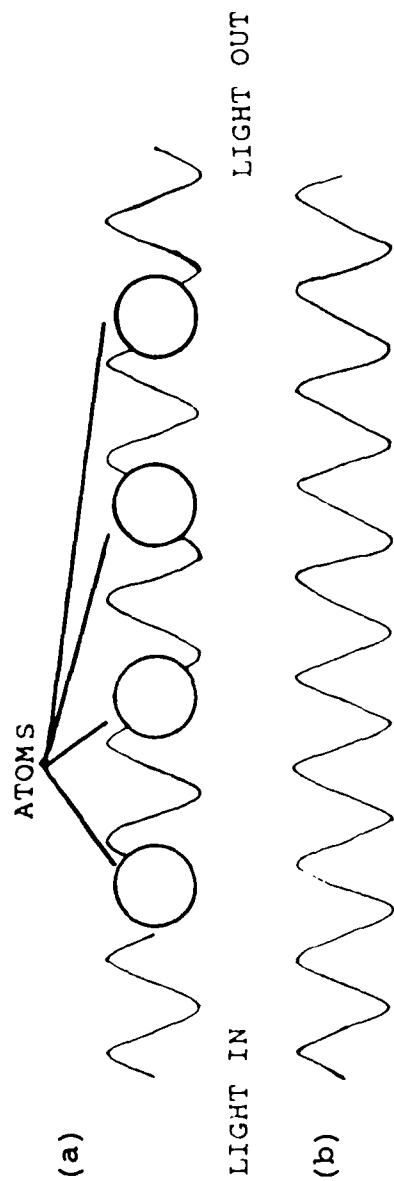


Figure 7 : Although the light beams a and b begin in phase, they are out of phase after beam a travels through the row of atoms. This is the origin of the index of refraction.

static electric field (E) distorts the charge distribution changing the dipole. When the electric field is small compared to the internal fields due to the electrons, the molecular polarizability (p), which is proportional to the dipole moment, can be described in a power series⁴⁹

$$p = p_0 + \alpha \cdot E + \beta \cdot \ddot{E}E + \gamma \cdot \ddot{E}EE + \dots \quad (1)$$

where α , β , γ are the static molecular polarizability tensors, respectively, the linear polarizability and the second and third-order hyperpolarizability. At lower field intensities (small E's) only the first term in equation 1 (α term) has an appreciable effect on p, and this is the case discussed in the earlier atomic example. As the field intensity increases, the second two terms (the second- and third-order hyperpolarizabilities, respectively) become more important. It is these latter two terms that are responsible for a molecule's nonlinear optical behavior. Physically, these terms represent a measure of the size of the nonlinear effect. That is, how easy it is to induce a polarization or equivalently, how tightly bound the electrons are to the nuclear framework. (The looser the binding, the further the electrons can be driven away from the nuclear framework resulting in a larger polarization and thereby, a larger nonlinear optical effect.) The above equation is modified for centrosymmetric molecules by the removal of the polarizability term p_0 (with a center of symmetry, there is no intrinsic polarizability) and removal of the second-order term ($\beta = 0$). Details are discussed below.

With the advent of the laser, large optical fields became available and it was natural to consider time-dependent fields. The equation describing the time-dependent molecular polarizability retains the notation of the static case for historical reasons,⁴⁹ i.e.,

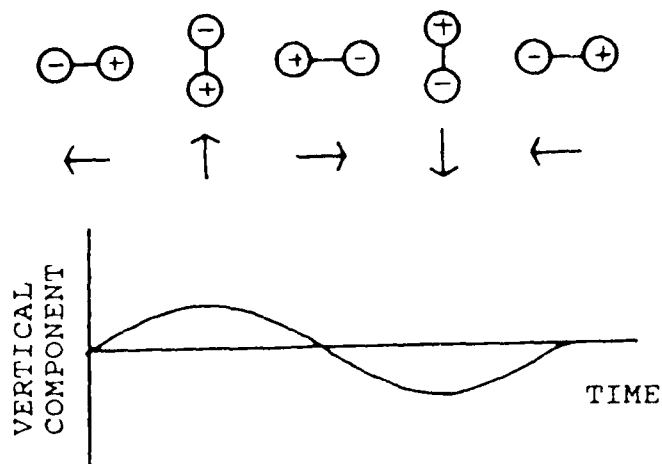
$$p = p_0 + \alpha(-\omega; \omega) \cdot E(\omega) + \beta(-\omega; \omega_1, \omega_2) \cdot \ddot{E}(\omega_1)E(\omega_2) + \gamma(-\omega; \omega_1, \omega_2, \omega_3) \cdot \ddot{E}(\omega_1)E(\omega_2)E(\omega_3) + \dots \quad (2)$$

where the coefficients are complex tensors and have frequency dependence. For example, the common linear polarization term $\alpha(-\omega; \omega)$ is composed of a real part, corresponding to the index of refraction, and an imaginary part, corresponding to absorption. The frequency dependent tensor notation uses negative signs to indicate conservation of momentum and subscript arguments to indicate the frequencies of the electric fields. For example, in second harmonic generation, the second-order microscopic polarizability tensor is represented as $\beta(-2\omega; \omega, \omega)$ or for the linear electro-optic effect (electric-field-induced-birefringence with a linear field dependence), $\beta(-\omega; 0, \omega)$.

We can obtain some important general information about the molecular properties associated with nonlinear optical effects by examining equation 2. First, consider an isotropic molecule

MOLECULAR DIPOLE MOMENT

(A) ROTATION



(B) VIBRATION

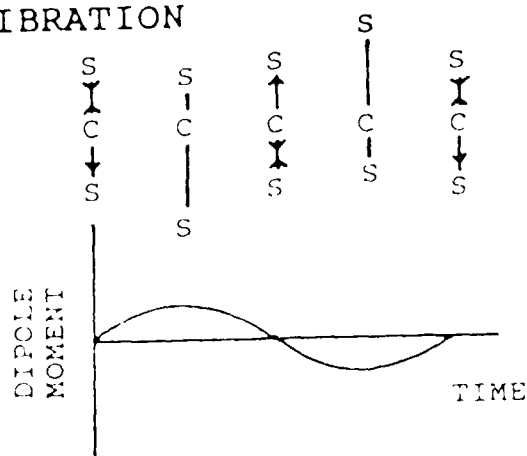


Figure 8: In (a) a noncentrosymmetric rigid rod molecule is used to demonstrate the origin of the molecular dipole. The arrows indicate the direction of the intrinsic dipole moment. In (b) the origin of the molecular dipole is shown to be due to vibrations in a centrosymmetric molecule, i.e., one that possesses a center of symmetry.

and the second-order hyperpolarizability term involved in second harmonic generation: $+P^{(2)} = \beta(-2\omega; \omega, \omega) \cdot E(\omega)E(\omega)$. For an isotropic molecule, β is independent of direction and therefore constant. Thus, if the axis direction is reversed ($x \rightarrow -x$, $y \rightarrow -y$, $z \rightarrow -z$) while leaving the electric field and the dipole moment unchanged in direction, the second-order term of equation 2 becomes, $-P^{(2)} = \beta(-2\omega; \omega, \omega) \cdot (-E(\omega))(-E(\omega)) = +P^{(2)}$. This can only be true if $+P^{(2)} = -P^{(2)}$, i.e., $\beta = 0$. In other words, centrosymmetric molecules only have contributions from odd-order terms in equation 2; they cannot exhibit even-order effects such as second harmonic generation.^{5, 8, 12, 17-21, 35, 41, 49-51, 53-56}

Second, it is clear that molecules with easily polarized electron clouds have the greatest potential for large nonlinear optical coefficients. Thus, we do not expect saturated organic molecules (i.e., those without π bonds) to exhibit much of a nonlinear optical effect: the bonding electrons are well localized so only small changes in charge distribution with changes in local field environments are expected.^{35, 41, 48-52} However, unsaturated, conjugated molecules with their large π electron delocalization should and do exhibit large nonlinear optical responses.^{17-21, 35, 41, 48-51} A more detailed look at the appropriate molecular properties for specific nonlinear responses is presented below.

SECOND-ORDER MOLECULAR PROPERTIES

The majority of work reported on organic nonlinear optical materials has focussed on second-order effects^{8, 12, 14, 17-21, 40-75} (molecules with large β coefficients in equation 2) for the obvious reason that the effect is larger than the third order response and therefore easier to measure. There exists a good understanding of the origin of this effect and how to optimize molecular and bulk material properties to enhance it.^{8, 12, 17-20, 35, 37, 38, 40-75} For organic molecules the general molecular properties that are required for good second-order nonlinear response are: noncentrosymmetry, planarity and delocalized electron systems.^{8, 12, 17-20, 35, 37, 38, 40, 41, 44, 45, 48, 54-68} Additionally, substituent groups that enhance the charge asymmetry of the molecule, i.e., strong electron donor and electron acceptor groups, lead to low-lying charge-transfer resonance states and thereby enhanced β 's.^{8, 12, 17-20, 40, 41, 54, 55, 57-59, 63, 69, 72-75} The charge asymmetry inducing substituents make it easier to polarize the molecule: the flow of charge is enhanced in one direction - like an "optical diode". (See Fig. 9).⁴⁹⁻⁵¹

In the following table, examples showing the importance of the above molecular properties in enhancing second-order effects are given.^{72, 73}

"OPTICAL DIODE"

π ELECTRON POLARIZABILITY ENHANCEMENT

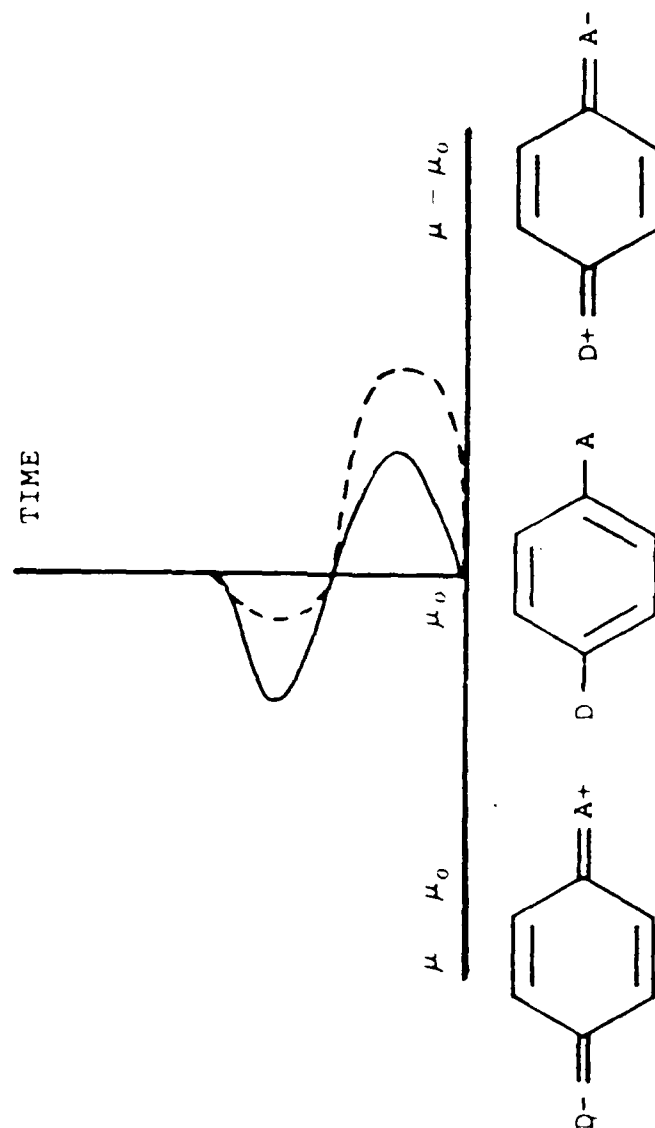
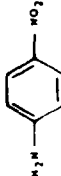

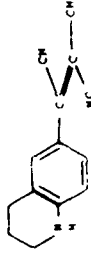
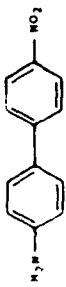
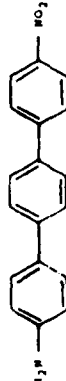
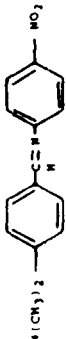
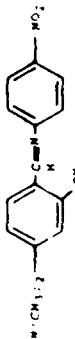
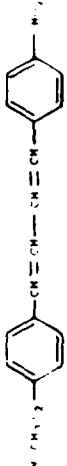


Figure 9: The solid line indicates the polarization induced in unsubstituted benzene; the substituted benzene response is given by the dashed line. (The μ 's are the dipole moments for the indicated resonance states.) Notice that the addition of donor and acceptor groups enhances the polarization of the π electrons in one direction vs the other - the "optical diode". This figure was adapted from Ref. 49.

TABLE 3

RELATION OF MOLECULAR STRUCTURE TO β

MOLECULE	$\beta \times 10^{-30}$ esu (1.9 μ m)	PROPERTY DESCRIPTION
	5.7	STANDARD
	21.4	MORE EFFECTIVE ELECTRON DONOR AND ACCEPTOR; NON PLANAR DONOR
	41.8	FORCED COPLANARITY VIA RING FORMATION
	20.1	INCREASED CONJUGATION
	50.7	INCREASED CONJUGATION
	23.4	NON-PLANAR
	61.6	PLANAR
	111.2	COMBINATION OF ALL MOLECULAR PROPERTIES

*Adapted from Refs. 72 and 73

THIRD-ORDER MOLECULAR PROPERTIES

The theory and understanding of third-order processes (where $\chi^{(3)}$ in equation 2 is significant) and their origin in organic molecules is still in its infancy but has seen remarkable progress over the past few years.^{6-11,14,18-20,34,37,38,48,52,76-89} The molecular origin of this effect is believed to be related to the correlated motion of electrons and to highly charge correlated virtual excitations (Fig. 10).^{58,10,18,20,37,38,48,74,76,78-80,84} The correlated motions are believed to arise from the combined action of electron-phonon and coulombic interactions.^{6,8,10,37,38,48,74,76,78-80,85} However, the magnitude of the electron-phonon coupling contribution is not clear.^{10,76}

Identification and characterization of the molecular properties which lead to enhanced third-order effects is under study. The most important molecular property appears to be planar conjugation. There is some evidence that ladder polymers (polymers formed using fused aromatic rings) may be superior to open chain polymers because of improved π orbital overlap.^{13,37,38,76,80-82} and it is predicted by some researchers that γ will not increase beyond that observed for 20-25 repeat units (~ 60 Å).^{6,37,38,76,78,79} There is also experimental evidence suggesting that the incorporation of certain heteroatoms into the conjugation length can dramatically increase the third-order effect.^{10,37,38,76,81,82} again through improved π orbital overlaps. Another property that may be important and that is under investigation is the effect of intermolecular bonding, e.g., hydrogen bonding.⁹⁰

Charge-induced asymmetry as a means for enhancing third-order effects remains a controversial issue: a great deal of electron delocalization may arise from charge-induced separations. Further experimental investigations are required in order to assess its importance.⁸⁶⁻⁸⁸

MATERIAL PROPERTIES

The polarization induced in a material by the application of an electric field, E , is described by

$$P = P_0 + \chi^{(1)}E + \chi^{(2)}EE + \chi^{(3)}EEE + \dots \quad (3)$$

where P is the material polarizability, P_0 is the intrinsic polarizability and $\chi^{(i)}$ are the macroscopic material coefficients known as the material susceptibilities. The macroscopic susceptibilities are related to the microscopic hyperpolarizabilities as shown below.

$$\chi^{(1)} = N\alpha F(\omega)^2 \quad (4)$$

$$\chi^{(2)} = N\beta F(\omega_1)F(\omega_2)F(\omega_3) \quad (5)$$

$$\chi^{(3)} = N\gamma F(\omega_1)F(\omega_2)F(\omega_3)F(\omega_4) \quad (6)$$

VIRTUAL EXCITATION: AN INTERMEDIATE ELECTRONIC STATE (V) WHICH CANNOT BE OBSERVED; A PHOTON IS NOT ABSORBED BUT INDUCES A DIPOLE IN THE MOLECULE WHICH IS THEN SAID TO BE IN A VIRTUAL STATE.

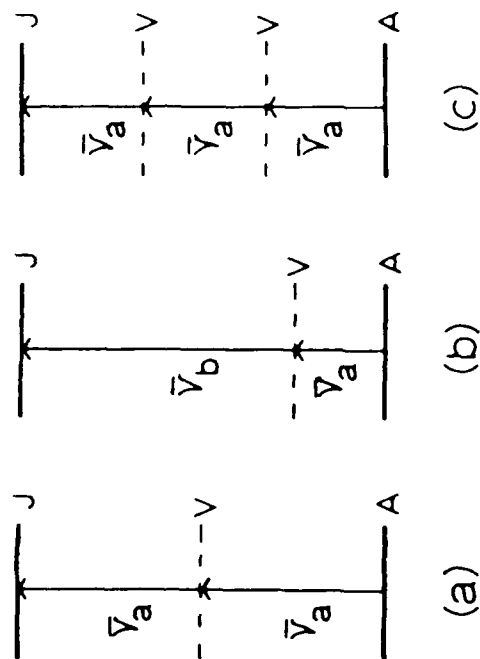


Figure 10: The absorption of two identical photons (a) and two different energy photons (b) via virtual states are shown. The absorption of three identical photons (c) via virtual states is also shown. A indicates a ground electronic state, J an excited electronic state and V a virtual state.





N is the number density of molecules and F is the local field factor at the specified frequency, i.e., the value of the electric field at the site of the molecule. F is a difficult quantity to estimate because of the mutual polarization of molecules in dense phases.^{49,50,57,61,93} Therefore, great care must be taken in relating microscopic and macroscopic quantities. This is especially true for equations relating $\chi^{(2)}$ to the second-order polarizability, β , because a detailed knowledge of the projection of the tensor onto the oriented molecule is required.^{17,41,49,50,57,93} Equation 5 is for the simplest case of a "rigid lattice-oriented gas" where all the molecules point in the same direction and are fixed in space.^{17,49,50}

Molecular orientation within a medium is an important aspect of both $\chi^{(2)}$ and $\chi^{(3)}$ nonlinear optical materials.^{12,17-21,43,53,56,63-66,72-74,91-94} The more ordered the molecules within the material, the larger the material response (see Fig. 11). The two most popular methods for ordering molecules in materials are, electric field poling,^{53,56,64,92-94} primarily used for $\chi^{(2)}$ materials, and Langmuir-Blodgett film deposition,^{43,66,95} used for both $\chi^{(2)}$ and $\chi^{(3)}$ materials.

Electric field poling works well for $\chi^{(2)}$ materials because of the required molecular charge asymmetry and its application to guest/host systems is diagrammed in Fig. 12. Initially, the guests are frozen in a random orientation in the polymeric host. The material is then heated to a temperature greater than the glass transition temperature of the host. This allows the guest molecules to rotate within the host. An electric field is then applied, causing the guest molecules to preferentially orient along the field direction. The material is cooled below the host's glass transition temperature, while maintaining the orienting electric field, thus freezing the guest molecules in an ordered, noncentrosymmetric orientation. The use of this technique to orient $\chi^{(2)}$ active side chains of main chain polymer backbones (Fig. 13) is also obvious and an area of active research.^{41,72,73,96-100}

While high degrees of order can be initially achieved using this technique, the molecular order does decay with time due to thermal relaxation and the inevitable increase in entropy of the system. Half-life for randomization can vary from a few days to a few years depending on the poling conditions and the particular molecules involved.^{53,100,101} A concentrated research effort is underway to increase half-lives.^{53,100,101} For example, adding functional groups to the pendant side chains⁹⁷ to serve as order preserving 'Hooks and Eyes' (Fig. 14), or dispersing the nonlinear optically active molecules in piezoelectric hosts where the intrinsic electric field⁹⁴ are methods being examined to help maintain the preferred intermolecular orientation.

Types of Molecular Packing

Packing	Type	Order	Magnitude
	Non-centric	Second	Moderate
	Non-centric	Second	Strong
	Centric	Third	Strong
	Centric	Third	Weak



 Direction of dipole moment

Figure 11: The effects of molecular packing on the magnitude of second and third order non-linear optical material properties are indicated above. The arrows indicate the direction of the dipole moment.

ELECTRIC FIELD POLING

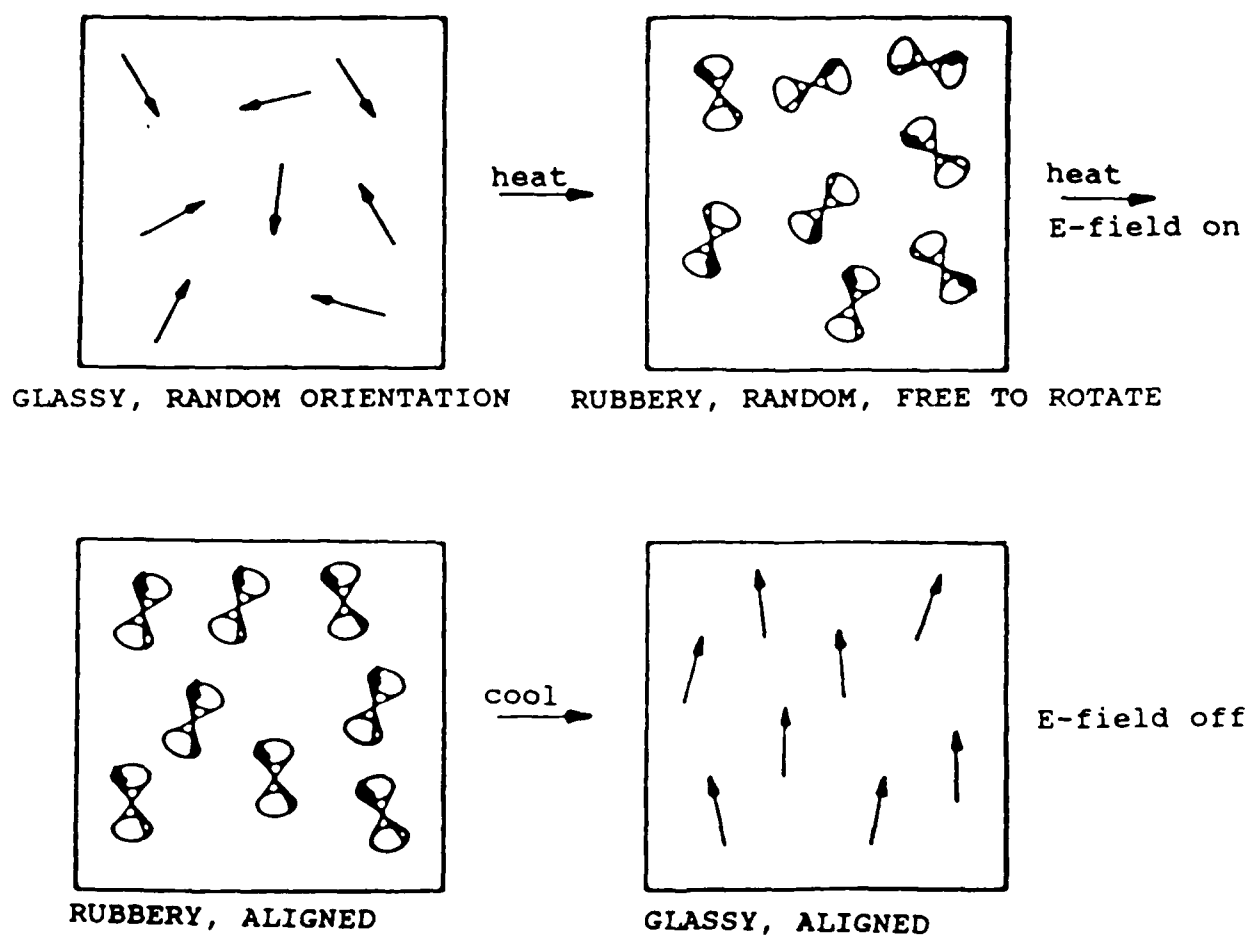


Figure 12: A graphic depiction of the electric field poling technique. In the first step, the composite material is heated above the glass transition temperature of the polymer host. An electric field is then applied to orient the molecules and the material is allowed to cool, freezing the guest molecules in a particular orientation. Adapted from Ref. 185.

ELECTRIC FIELD POLING OF LIQUID CRYSTAL SIDE CHAIN POLYMERS

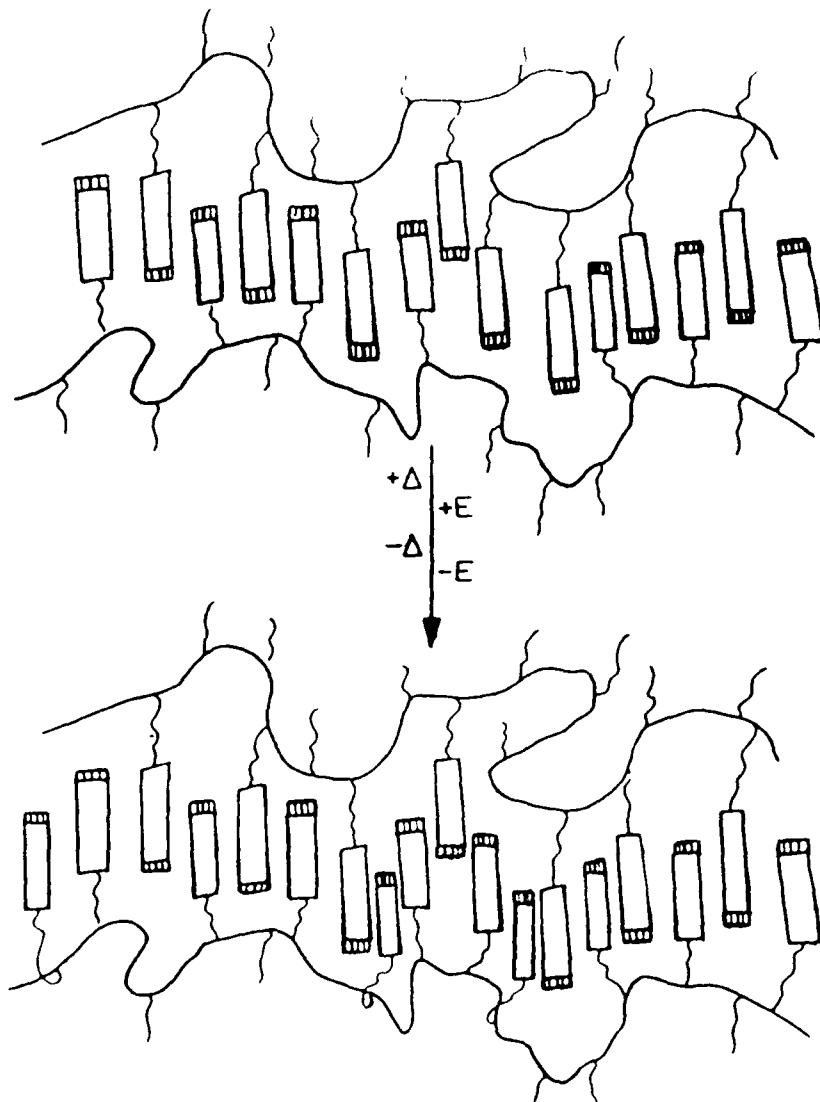


Figure 13: The electric field poling technique applied to liquid crystal side chain polymers. The rectangles represent the nonlinear mesogens; the hatched boxes are to assist in indicating orientation.

CHEMICAL "HOOKS AND EYES"



Figure 14: Chemical "Hooks and Eyes" could be used to assist in maintaining the orientation of the non-linear mesogenic pendant groups (the rectangular boxes as in Fig. 13) of liquid crystal side chain polymers after poling. Such a concept could be based on strong photo-induced covalent bonds (crosslinking) or weaker hydrogen bonding.

The Langmuir-Blodgett deposition technique allows for monomolecular control of orientation and composition.^{43,66,95,102-107} This technique requires surface active molecules i.e., molecules with hydrophilic and hydrophobic ends, and is useful in preparing both $\chi^{(2)}$ and $\chi^{(3)}$ materials. The technique is diagrammed in Fig. 15. The surface active molecules are spread onto the surface of the water and compressed to form a monomolecular film. Then, by repeated dipping, monomolecular film layers can be deposited onto a substrate. Unfortunately, Langmuir-Blodgett films are often contaminated with crystallite regions causing unacceptable amounts of light scattering.^{95,102-104}

MATERIAL MEASUREMENTS: $\chi^{(2)}$ MATERIALS

There are several experimental methods available for measuring/characterizing second-order nonlinear optical materials.^{108,109} Several of these methods are listed below and diagrams (Figs. 15-20) describing the techniques are shown on the following pages along with some of their advantages and disadvantages. The choice of characterizing method depends on the type of descriptive information desired and the physical form of the material.

$\chi^{(2)}$ CHARACTERIZATION METHODS

SECOND HARMONIC GENERATION
SINGLE CRYSTAL SECOND HARMONIC GENERATION
EFISH
POLYMER POLING
ELECTRO-OPTIC EFFECT

MATERIAL MEASUREMENTS: $\chi^{(3)}$ MATERIALS

Experiment complexity dramatically increases when making measurements on $\chi^{(3)}$ materials as compared to $\chi^{(2)}$ materials:^{78,79,109} all materials, ranging from air to the sample holder, can exhibit third-order effects (there are no symmetry restrictions)^{17,18,20,34,35,41} and the effect is small while the sample materials are often of poor optical quality.^{14,88,46,81,82} In addition, the experimenter must be concerned with resonant vs. nonresonant effects and, in some measurement methods, with the origin of the intensity dependent index of refraction, n_2 .^{9,11,29,81,82,110,111} Before describing a few of the methods available for measuring $\chi^{(3)}$ materials, resonant enhancement and intensity dependent refractive indices will be briefly discussed.

$\chi^{(3)}$ may be expressed as the sum of two types of susceptibilities due to resonant (R) and nonresonant (NR) contributions^{10,17,18,20,110}

$$\chi^{(3)} = \chi^{(3)}_R + \chi^{(3)}_{NR} \quad (7)$$

LANGMUIR-BLODGETT TECHNIQUE

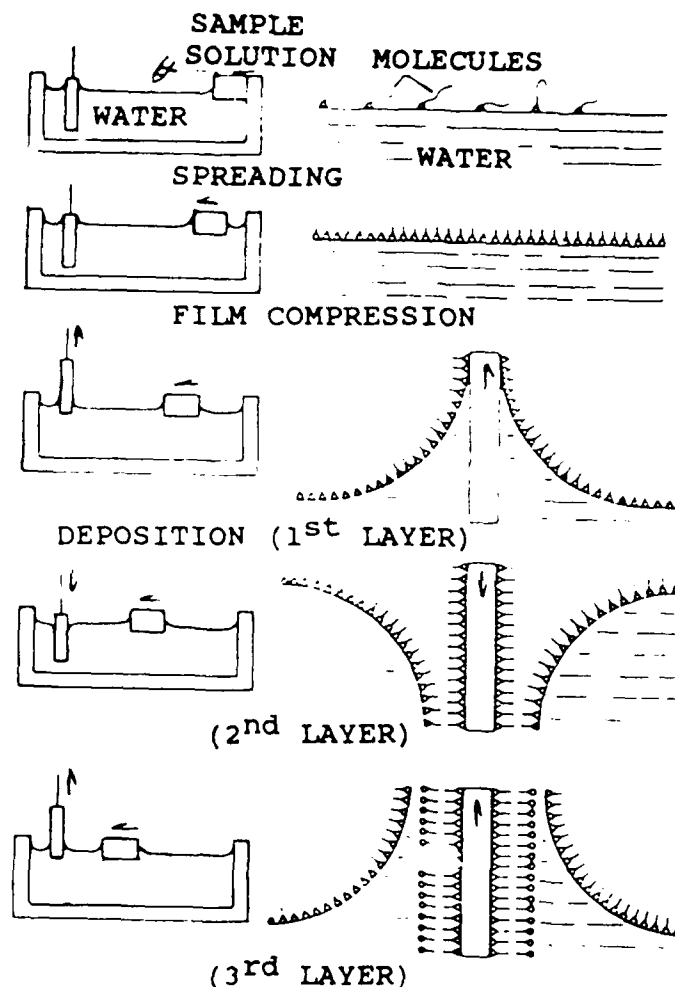
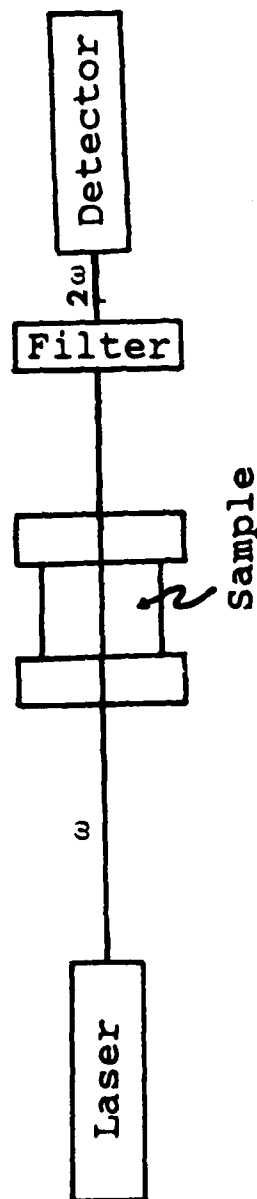


Figure 15: A descriptive outline of the production of a thin-film using the Langmuir-Blodgett technique.

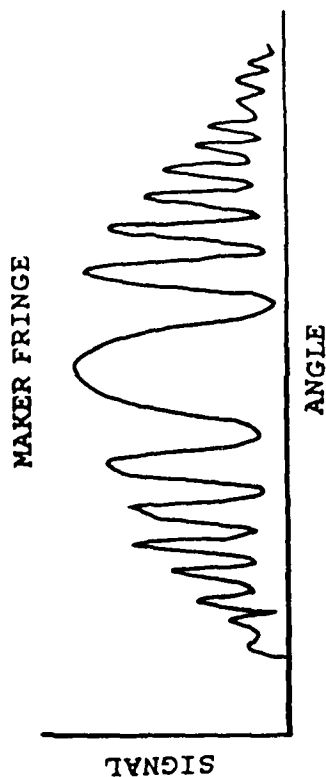
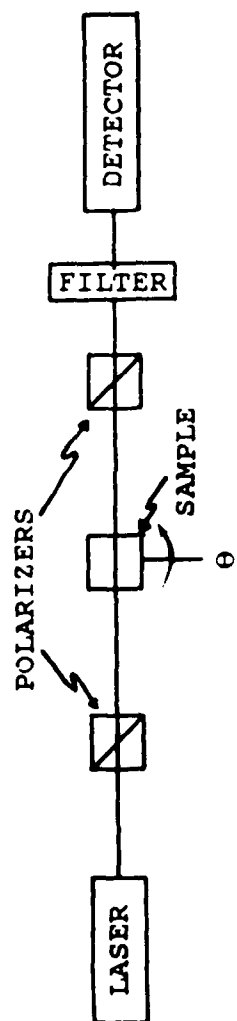
POWDER SHG



MATERIAL FORM: MICROCRYSTALLINE POWDER
ADVANTAGES: USEFUL FOR SCREENING
DISADVANTAGES: CANNOT RESOLVE MICRO- AND MACROSCOPIC
CONTRIBUTIONS TO OPTICAL NONLINEARITY

Figure 16

SINGLE CRYSTAL SHG

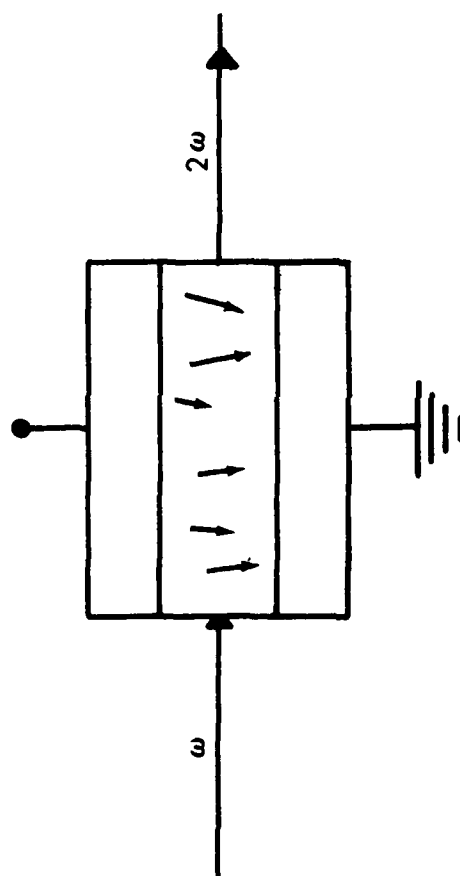


MATERIAL FORM: LARGE SINGLE CRYSTAL (mm to cm)
ADVANTAGES: MEASURES TENSOR ELEMENTS OF χ^2
DISADVANTAGES: REQUIRES CRYSTAL POLISHING AND ORIENTATION, KNOWLEDGE OF INDICES OF REFRACTION

Figure 17

ELECTRIC FIELD INDUCED SECOND HARMONIC GENERATION

(EFISH)



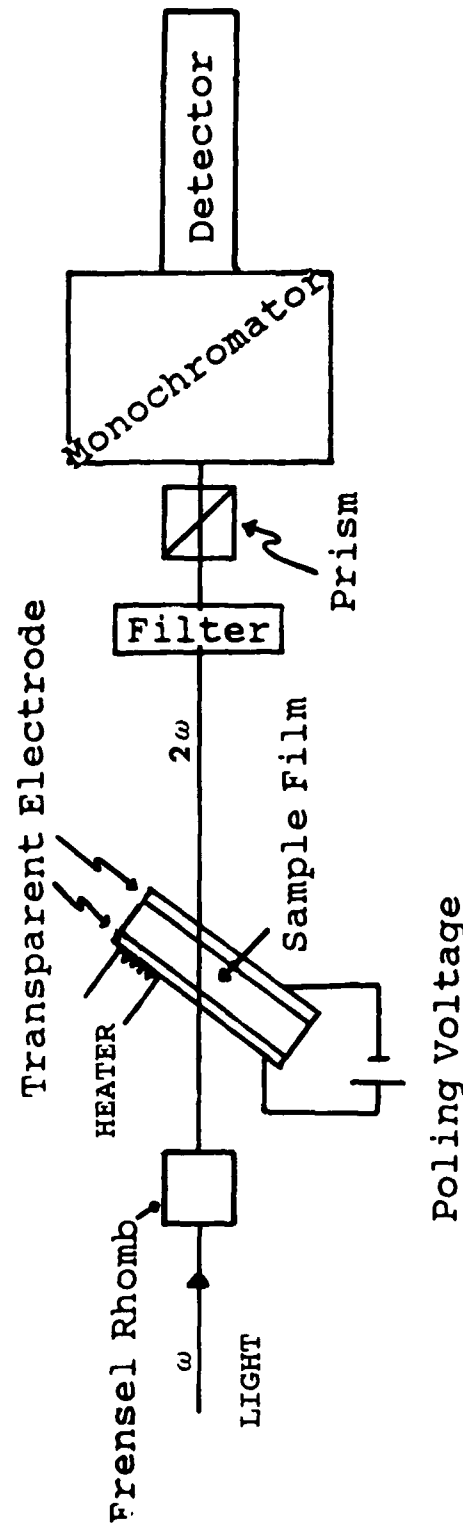
MATERIAL FORM: SOLUTION (LOW POLARITY SOLVENTS)

ADVANTAGES: OBTAIN MOLECULAR PROPERTIES,
RELATIVE COMPARISONS POSSIBLE

DISADVANTAGES: MOLECULAR PROPERTIES ARE SUBJECT TO ENVIRONMENT

Figure 18

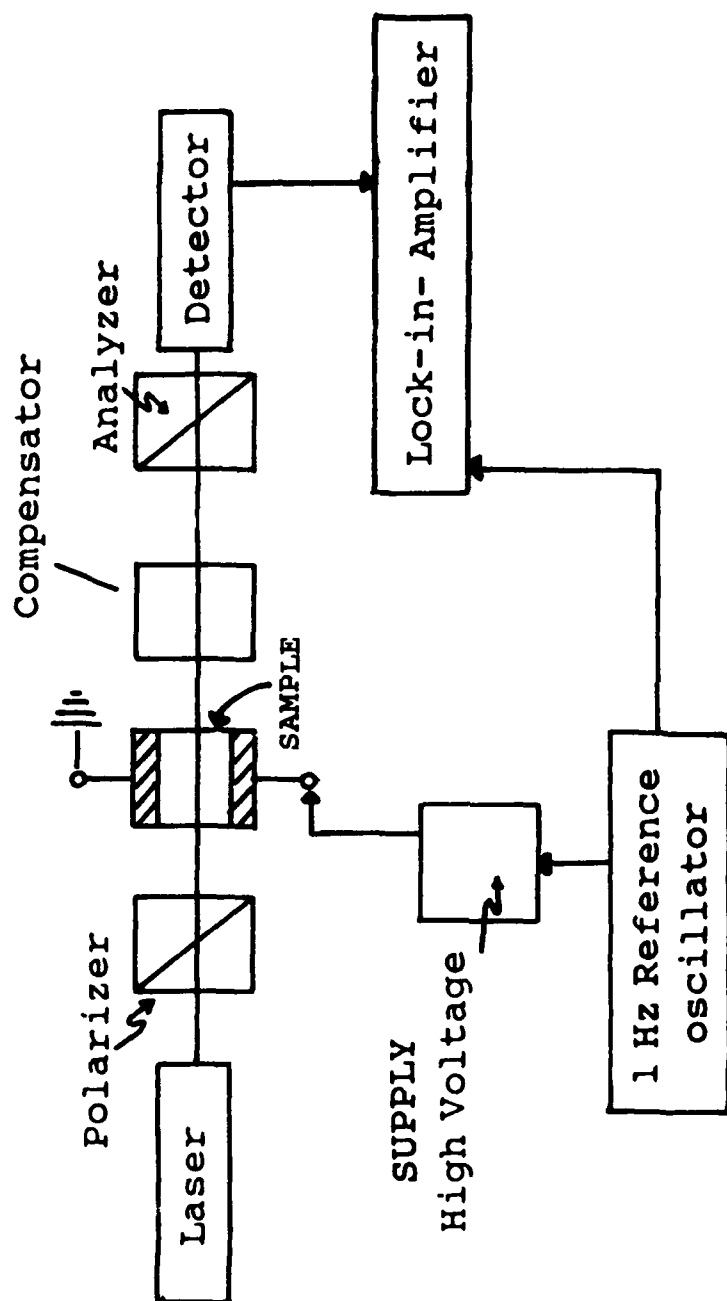
POLYMER POLING



MATERIAL FORM: POLYMER SYSTEM
ADVANTAGES: REAL LIFE ENVIRONMENT, EASY SIGNAL DETECTION
DISADVANTAGES: NOT A DIRECT MEASUREMENT FOR ELECTRO-OPTICS

Figure 19

ELECTRO-OPTIC EFFECT



MATERIAL FORM: POLYMER SYSTEMS, CRYSTALS
 ADVANTAGES: DIRECT MEASUREMENT (in device form)
 DISADVANTAGES: LESS SENSITIVE THAN SHG
 NOT AN IN-SITU TEST
 CRYSTALLOGRAPHIC ORIENTATION FOR CRYSTALS

Figure 20

The nonresonant susceptibility contributions occur in spectral regions far from any optical absorption of the material, while resonant contributions occur at frequencies near or resonant with the material's optical absorptions. Resonance effects are usually measured at absorption band edges and can cause considerable enhancement of the nonlinear optical susceptibility through admixtures of excited state properties and contributions from excited state dynamics. For materials of interest in eye/sensor protection, the nonresonant effects are of greatest interest because they are responsible for broadband response with good transparency at ambient light levels.

Another important aspect of $\chi^{(3)}$ materials is the intensity dependent refractive index, n_2 . At high irradiance levels, a material's index of refraction can be described by

$$n = n_0 + n_2(I) \quad (8)$$

where n_0 is the linear refractive index and n_2 is the intensity dependent refractive index.^{9,11,29,110,111} At nonresonant optical frequencies, n_2 can arise from any of the mechanisms listed in the following table.^{9,29,81,82,110}

TABLE 4
MECHANISMS OF NONRESONANT SELF-INDUCED INDEX CHANGES

MECHANISM	n_2 (esu)	τ (sec)
MOLECULAR-ORIENTATION KERR EFFECT	$10^{-11} - 10^{-12}$	$10^{-11} - 10^{-12}$
MOLECULAR-REDISTRIBUTION (LIBRATIONS)	$10^{-12} - 10^{-13}$	$\sim 2 \times 10^{-13}$
NONLINEAR ELECTRONIC POLARIZABILITY	$10^{-8} - 10^{-14}$	$10^{-14} - 10^{-15}$
ELECTROSTRICTION	$10^{-11} - 10^{-12}$	$10^{-8} - 10^{-9}$
THERMAL EFFECTS	$10^{-4} - 10^{-5}$	$10^{-1} - 1$

Of these mechanisms, the nonlinear electronic polarizability is the most important for eye/sensor protection due to its fast response time. While the molecular-orientation Kerr effect (quadratic electric-field-induced-birefringence) is also fast, it suffers from a saturation effect at high light intensities due to the complete orientation of molecules.^{110,112}

There can also be a resonant contribution to n_2 when near a strong absorption frequency. At resonant or near resonant frequencies, some of the light is absorbed which causes a redistribution of the material's electronic energy levels.^{8,10,29,110} This results in a change in the dispersion associated with the absorption band, a resonant enhanced intensity dependent index of refraction. Such an effect is in general not compatible with the broadband response required for

an eye/sensor protection device.

Of the characterization methods listed below and diagrammed in the following pages (Figs. 21-25), only third harmonic generation does not depend on n_2 .^{81,82,109,112-116} As before, the sample form and the type of information desired dictate the appropriate characterization method.

$\chi^{(3)}$ CHARACTERIZATION METHODS
DEGENERATE/NONDEGENERATE FOUR WAVE MIXING
M-LINE TECHNIQUE
SURFACE PLASMON TECHNIQUE
OPTICAL KERR EFFECT
THIRD HARMONIC GENERATION

MATERIALS PROGRESS

$\chi^{(2)}$ Materials

Most of the organic material development work has involved $\chi^{(2)}$ systems: organic crystals, guest/host type structures, liquid crystal side chain polymers and liquid crystal polymers.^{8,14,17,19,21,37,38,40-75,100,117} Of these general types, the latter three are of greatest interest because of the difficulties associated with growing reproducible, high optical quality crystals and the accompanying processing problems.^{12,118} Van der Waals crystals are formed by dipolar forces between molecules and so, good second-order molecules with their large dipole moments are difficult to assemble into a noncentrosymmetric bulk crystal.¹² Researchers are examining different approaches to crystal growth using forces stronger than van der Waals attractions such as hydrogen bonding and molecular salts.^{17,41}

Non-crystalline organic materials appear to be promising at this time: $\chi^{(2)}$ values on the order of 10^{-7} esu have been reported with response times on the order of microseconds.^{14,37,38,96,98,100} The majority of work in this arena has focussed on guest/host type structures where the second-order molecule is a guest in a polymer host, e.g., an azo-dye in poly(methyl methacrylate).^{12,64,93,176} One particularly interesting example of this type of system is the use of a crystalline copolymer of vinylidene fluoride and trifluoroethylene as the host and an aminoazo compound as the guest.⁹⁴ In this case, the host is a ferroelectric composite with electric fields of 10^6 V/cm permanently induced in the amorphous regions containing the guest molecules.⁹⁴ This should lead to saturation orientation of the guest molecules^{57,94} and thereby a large $\chi^{(2)}$.

A significant amount of work has also been reported involving Langmuir-Blodgett films of highly polarizable molecules.^{40,43,66,95,103-107}

DEGENERATE FOUR WAVE MIXING

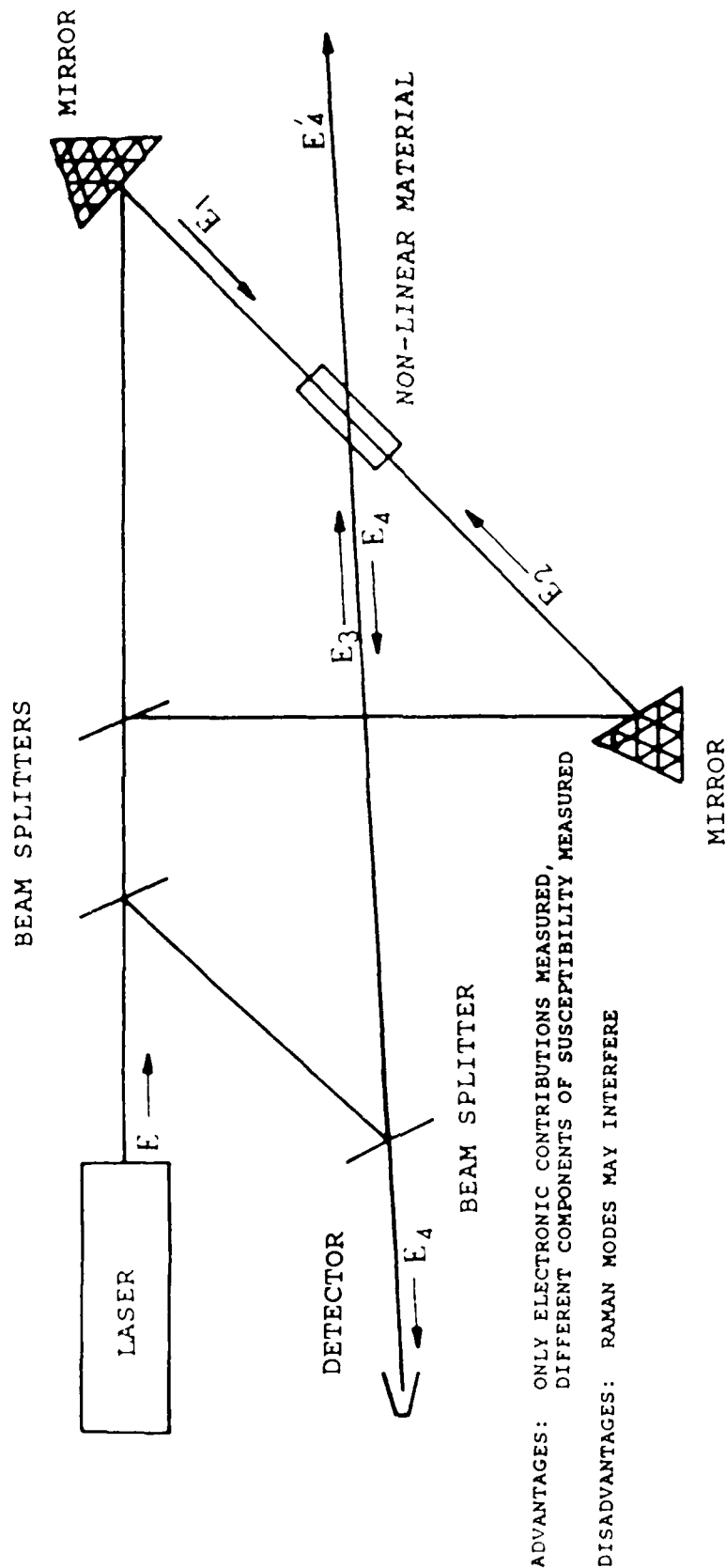


Figure 21: A schematic diagram of the degenerate four wave mixing technique. Beams E_1 and E_2 are known as the pump beams and E_3 is the probe beam. These three beams interact in the nonlinear medium to produce a phase-conjugate beam (E_4) which propagates exactly opposite to the probe beam (see Fig. 31). The term degenerate is applied to this technique if all of the beams have the same frequency.

M-LINE TECHNIQUE

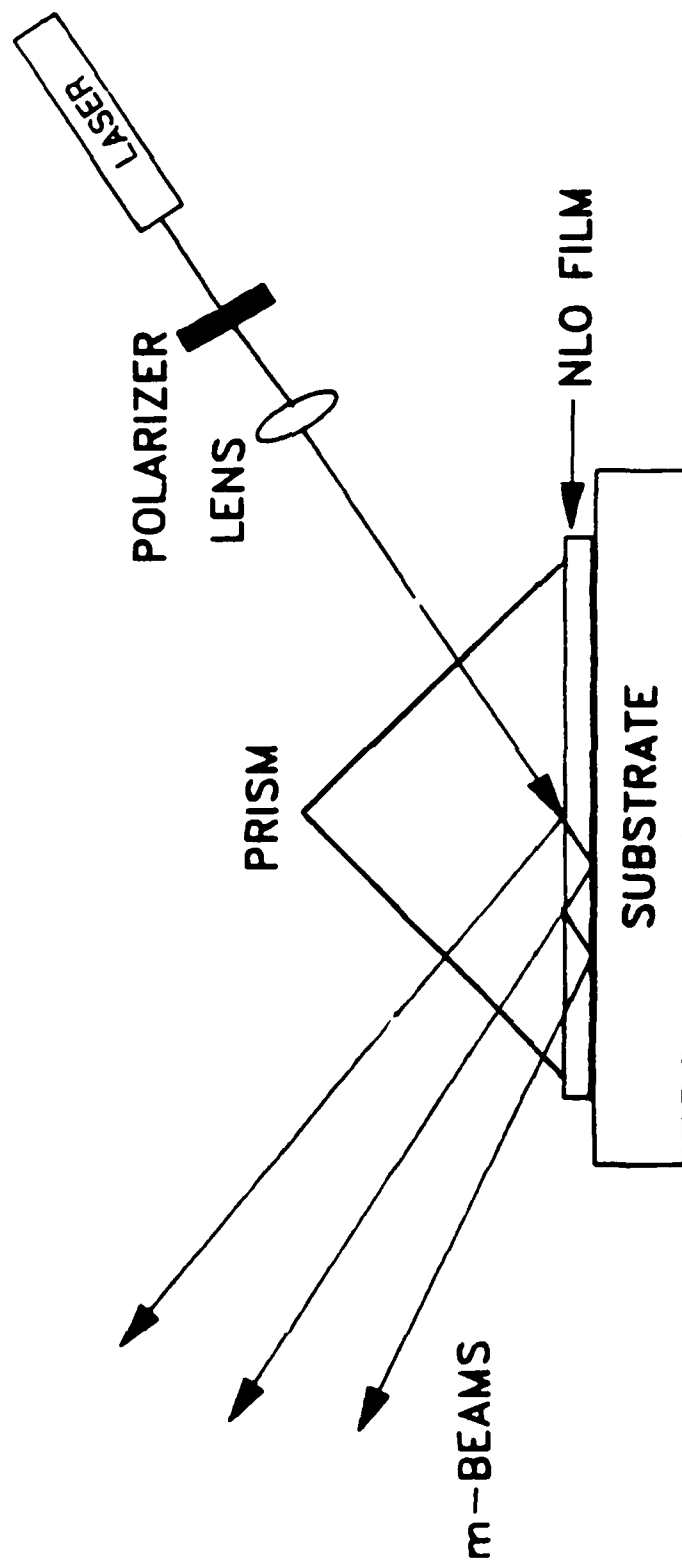


Figure 22: In this technique, the nonlinear optical film acts as a quasi-waveguide where leaky modes are excited. By measuring the angles associated with the m-lines, an accurate index of refraction and film thickness can be obtained. Information (sign and magnitude) on n_2 and $\chi^{(3)}$ can be obtained by varying the laser intensity and monitoring changes in the m-line angles.

SURFACE PLASMON

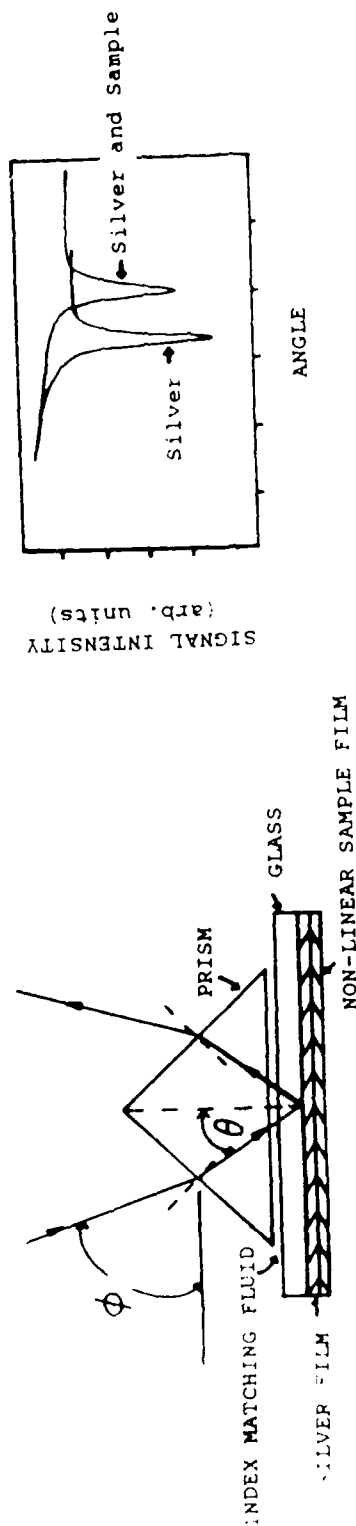


Figure 23: Surface plasmons are electromagnetic waves which propagate along the metal and sample film. At a certain angle, the incident light couples to the interface as a surface plasmon and signal intensity drops. Knowing this angle, it is possible to obtain information on the dielectric constant and the index of refraction of the sample. In nonlinear optical materials, the coupling angle depends on the light intensity and this intensity dependence gives the magnitude of n_2 and thereby $\chi^{(3)}$. A particular advantage to this technique is that the sign of n_2 and $\chi^{(3)}$ are obtained.

OPTICAL KERR EFFECT

ADVANTAGES: ONLY REAL PART OF SUSCEPTIBILITY MEASURED,
DETERMINE MAGNITUDE AND TIME RESPONSE OF NONLINEARITY

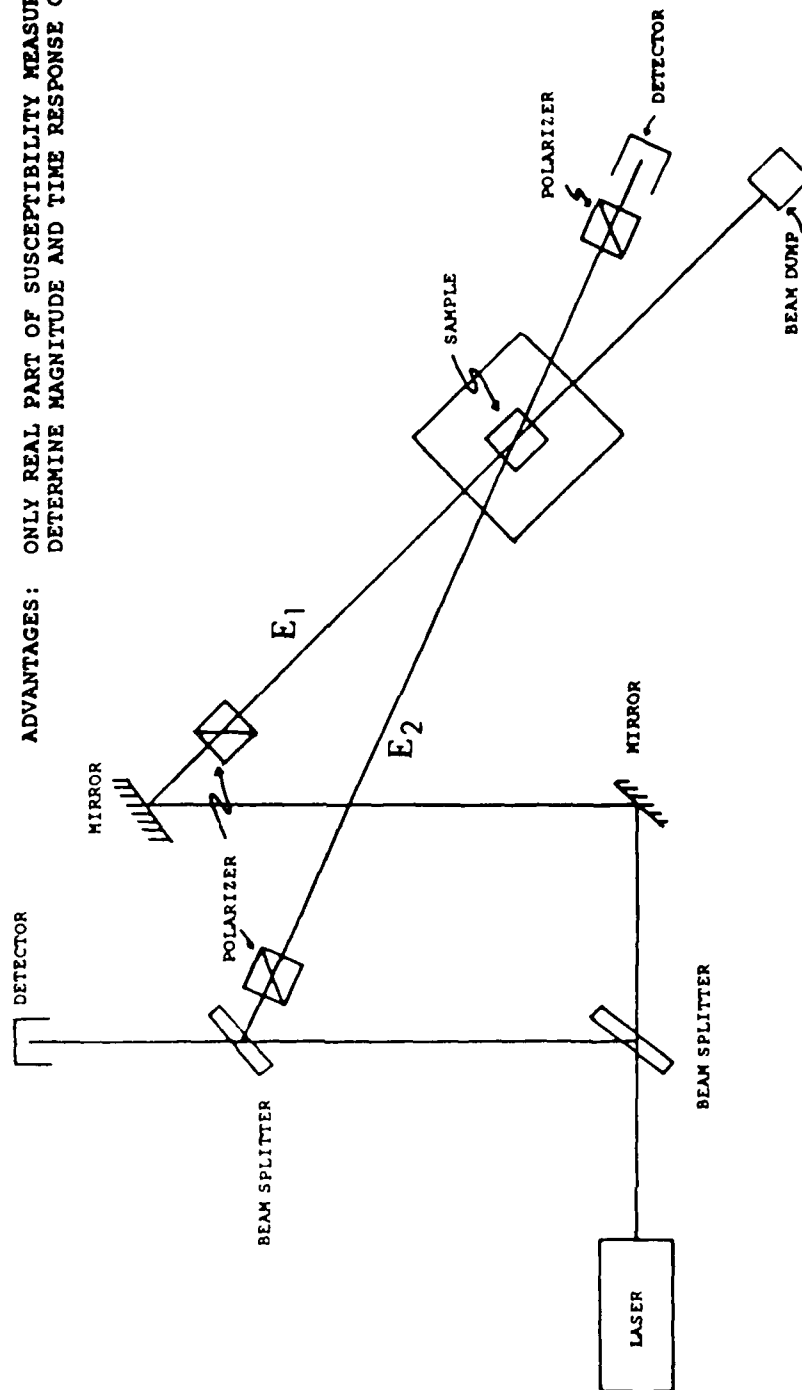
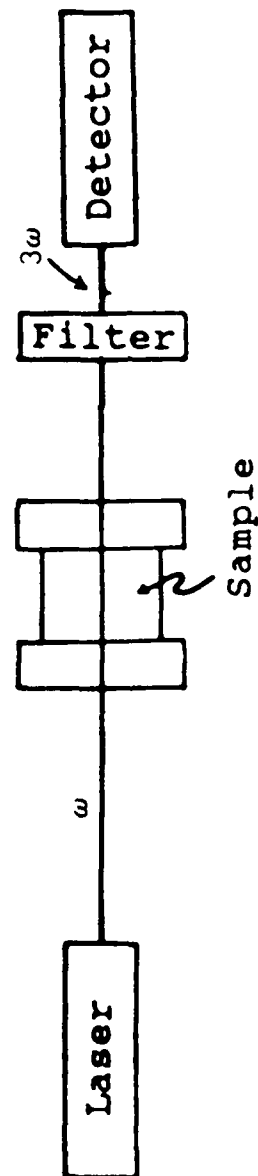


Figure 24: In this characterization technique, a pump beam (E_1) induces a birefringence in the nonlinear optical material. This induced birefringence alters the polarization of the probe beam (E_2). The pump and probe beams are oriented at 45 degrees so that the probe beam components experience different indices of refraction.

THIRD HARMONIC GENERATION



ADVANTAGES: SENSITIVE SCREENING TECHNIQUE,
NONRESONANT MEASUREMENT

DISADVANTAGES: INDIRECT MEASUREMENT OF SUSCEPTIBILITY
OF INTEREST

Figure 25

However, probably the most promising area of organic material development involves liquid crystal side chain and liquid crystal main chain polymers.^{8,14,37,38,57,99,100,117,119-121} Liquid crystal side chain polymers are formed by attaching mesogenic units to polymer backbones using spacer groups to decouple motion of the side chain from the backbone (See Fig. 26).^{41,119-121} An electric field is used to orient the side chains. $\chi^{(2)}$ values on the order of 10^{-9} esu have been reported with response times on the order of microseconds for these kinds of materials.^{14,37,38,96,98} Preliminary results showing GHz modulation (nanosecond response times) have also recently been reported, but not published.^{14,96,98}

On the other hand, main chain liquid crystal polymers¹¹⁹ (also known as polar polymers) have demonstrated substantially enhanced second-order effects as compared to their monomers.⁵⁷ This enhancement is theorized to arise from the structural ordering of the monomers. Further enhancement may be possible by orienting the polymer chains themselves (see the discussion in Proposed Future Research Efforts).

A major focus of future $\chi^{(2)}$ research will be to develop materials with $\chi^{(2)}$ oriented parallel to the material surface rather than perpendicular.^{14,37,38,98} Such a development would allow for greater usable surface areas and possibly thinner films than are currently available. Both are advances that would make meeting the optical requirements for eye/sensor protection devices more realistically attainable.

An extensive compilation of $\chi^{(2)}$ materials and their properties can be found in reference 19.

$\chi^{(3)}$ Materials

Although the origin of third order effects is not fully understood, progress has been made in developing materials with useful $\chi^{(3)}$ properties.^{9-11,16,18,20,37,38,85,89,122-141} Organic $\chi^{(3)}$ materials can be somewhat arbitrarily divided into four main classes: fused ring polymers, long chain unsaturated polymers, organometallic polymers and miscellaneous. Appendix A contains a brief compilation of reported $\chi^{(3)}$ materials for each of these areas and an additional area, inorganics, included for comparison.

The largest reported $\chi^{(3)}$ values are for long chain unsaturated polymers, specifically the poly(diacetylene) (PDA) materials, which have received extensive attention.^{9,16,34,111,122-139} A wide variety of substituent groups to the main chain have been studied, but overall, PDA materials are highly absorbing in the visible region of the spectrum and the reported values of $\chi^{(3)}$ are resonant-enhanced; undesirable qualities for eye/sensor protection. However, steady advances in the magnitude of the third-order effect have

LIQUID CRYSTAL SIDE CHAIN POLYMERS

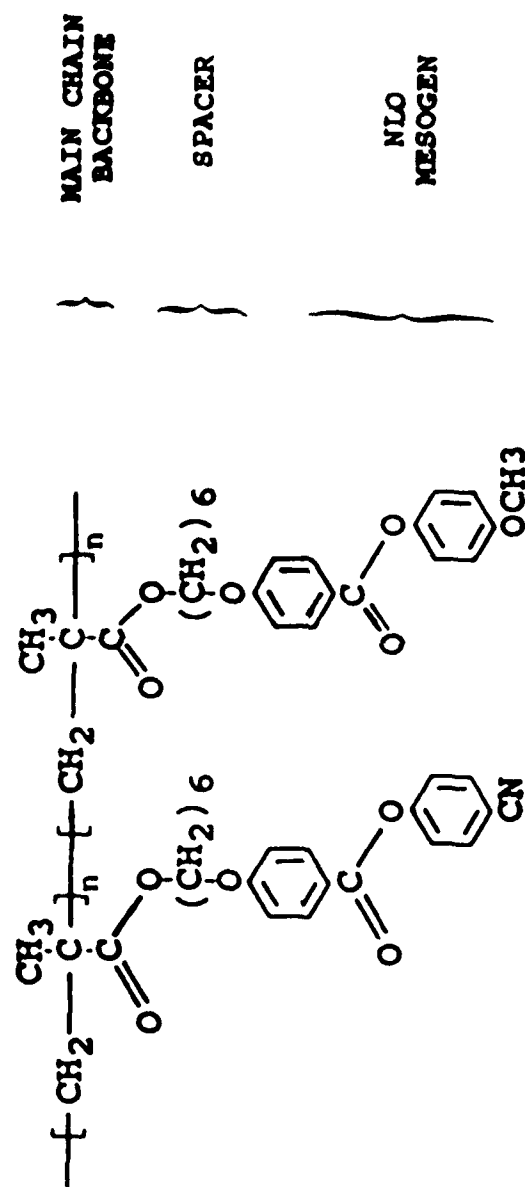


Figure 26: A schematic diagram of a liquid crystal side chain polymer.

been reported.^{9,34,111,123,131,132}

Recent investigations of ladder polymers and rigid-rod polymers have reported nonresonant $\chi^{(3)}$ values on the order of 10^{-9} esu and are a promising new area of research.^{9,10,13,37,38,44,78-80,140-142} These large nonlinear effects are believed to arise from increased π orbital overlap, as compared to open chain polymers.^{13,37,38,76,78-80} Current research efforts are focussing on the effects of substituent groups and heteroatom substitution, which preliminary results suggest may dramatically increase the optical nonlinearity.^{9,37,38,78,80,81,82,89}

An exciting new area in organic $\chi^{(3)}$ material development is organometallics.¹⁴³⁻¹⁴⁵ The incorporation of inorganic components into organic polymer systems has produced $\chi^{(3)}$ values on the order of 10^{-10} esu.¹⁴³⁻¹⁴⁵ Investigations into the effects of different inorganic components in these materials are currently underway.¹⁴³⁻¹⁴⁵ Inorganic/organic guest/host systems have also shown third-order effects but the magnitude is not clear.

Among the miscellaneous $\chi^{(3)}$ materials, small metal particles in colloidal suspensions,¹⁴⁶ azo dye attached copolymers¹⁴⁷ and dye doped glasses^{148,149} have all exhibited rather large $\chi^{(3)}$ and n_2 values.

Future research efforts on organic $\chi^{(3)}$ materials are being directed at developing a fuller understanding of the origin of the third-order effect via small systematic changes on the molecular level, i.e., trial and error.^{37,38,81,82} Concomitantly, material development will occur. The other major research thrust will be in developing materials with better optical properties as well as improved mechanical and processing properties.^{14,37,38} These latter properties are critical to the development of useful protection devices.

DEVICE CONCEPTS

Material Capabilities

In this section generic eye/sensor protection devices that make use of nonlinear optical materials are described. It is generally agreed that $\chi^{(2)}$ materials have now developed to the point where they can compete with their inorganic analogs in the areas of optical communication and computing devices ($\chi^{(2)}$ $\sim 10^{-7}$ esu).^{37,38,45,88} However, with respect to eye/sensor protection, devices based on $\chi^{(2)}$ materials generally involve the linear electro-optic effect or frustrated internal reflection and are relatively slow to respond (msec to nanosecond time scale).^{14,64,88,93,117,150} While such a response time may be adequate for protection against CW laser irradiation, it is not adequate for pulsed laser irradiation protection. In addition, electro-optic devices usually require

high voltage power sources; they are not passive devices. Therefore, most recent proposals for eye/sensor protection devices employ designs based on electronic polarizable $\chi^{(3)}$ materials (see Table 4).

State-of-the-art third-order electronic materials have $\chi^{(3)}$ s that are on the order of 10^{-9} esu.^{14,37,38,78,79,81,82,160} If improvements in the optical quality (reduced scattering and absorption) of these materials can be made, they may find application in optical wave guide devices. However, before they find broad device applications, $\chi^{(3)}$ must be increased by at least two orders of magnitude.^{14,37,38}

Device Designs

In the following section and figures, device designs based on $\chi^{(2)}$ and $\chi^{(3)}$ materials are described.

The first concept (Fig. 27) involves the linear electro-optic effect. This effect is associated with $\chi^{(2)}$ materials that are placed in an electric field. The applied field causes the material to become anisotropic and birefringent. The proposed eye/sensor protection device places the material between crossed polarizers. (A nonlinear optical solution/liquid would be housed in a material cell located between the crossed polarizers.) In the absence of an applied field, the crossed polarizers completely attenuate any incident light. Applying an electric field causes the nonlinear material to rotate the plane polarized light coming through the incident polarizer allowing some light to pass through the exiting polarizer. The maximum throughput is limited to 50% because the incident light must first be polarized and this attenuation is too great for eye protection systems. In addition, an adequate response time has not been demonstrated for these materials. For guest/host materials, the response time is on the order of microseconds (nanosecond response times have been reported but not published).^{98,194} For liquid or solution samples, the effect can be fast for small molecules, on the order of tens of nanoseconds, but as the size of the active molecule increases so does the response time. Additionally, the response time for these types of devices will depend on overcoming the difficulties associated with generating fast electronic pulses in the kilovolt range.

Liquid crystals and ferroelectric liquid crystals have shown promising results when incorporated into linear electro-optic devices,¹⁵¹⁻¹⁵⁸ but suffer from the same disadvantages listed above.

LINEAR ELECTRO-OPTIC DEVICE

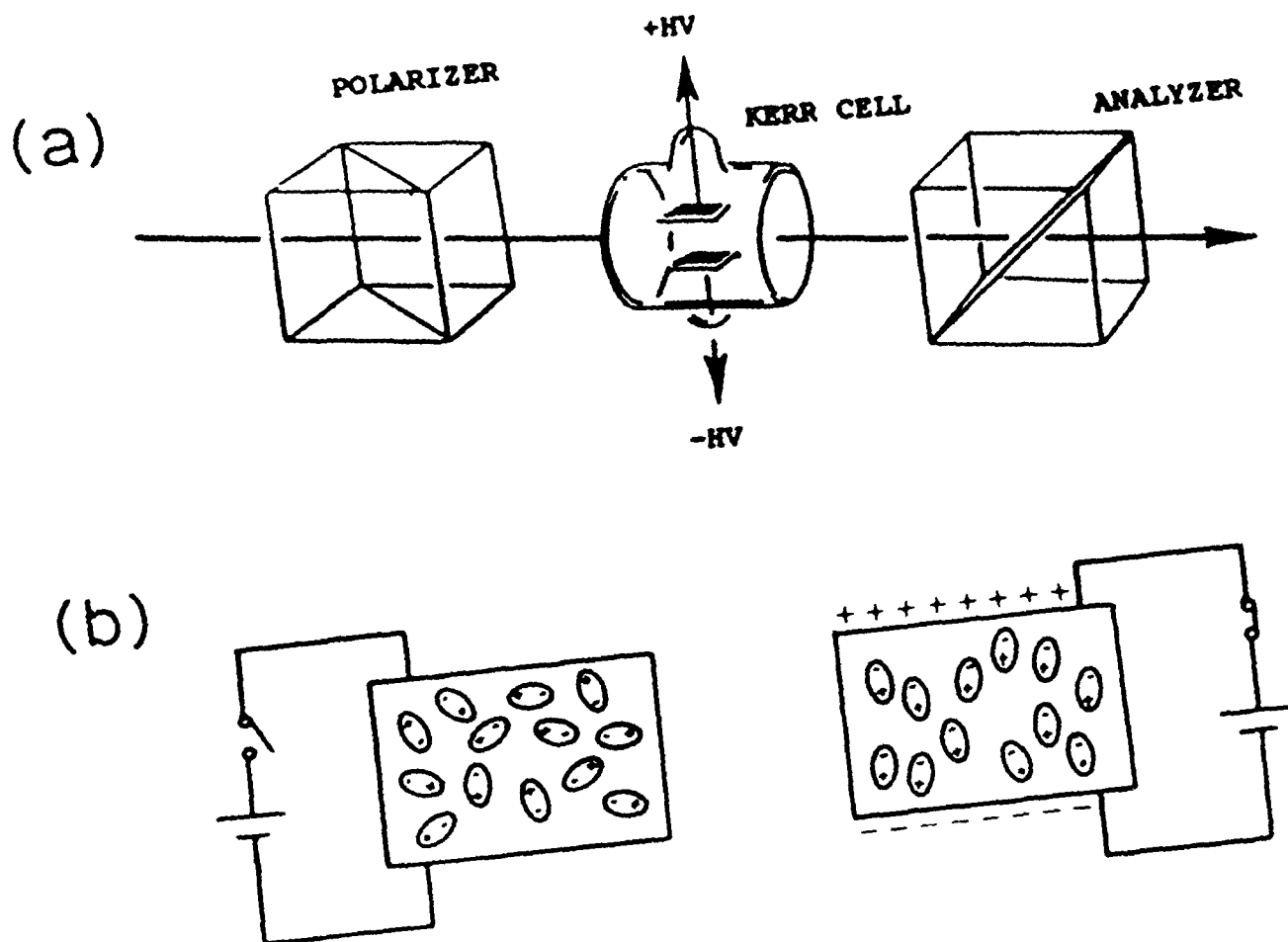


Figure 27: Linear Electro-Optic Device: (a) diagrams the optical train and (b) indicates how the device works. The ovals in (b) represent polar molecules which change from a random orientation to an aligned one when an electric field is applied thereby inducing a birefringence which rotates the plane of polarization of the incident light.

As diagrammed in Fig. 28, a device similar to the linear electro-optic one described above can be designed making use of the optical Kerr effect. For the system diagrammed, again the response time depends on the rate of reorientation of the active molecules.

A slight variation in this theme is the liquid crystal composite. In this device, small droplets of liquid crystals are dispersed in a polymeric host. The application of an electric field causes the liquid crystals in the droplets to align making the material transparent. This device requires the refractive indices of the polymeric host and the oriented liquid crystal to match. As the electric field is reduced, the liquid crystals assume a more random orientation and a refractive index mismatch occurs resulting in increased scattering - the material becomes a milky white color. The process is reversible and easily adapted to device design. However, the response time of the device is on the order of milliseconds, too slow to protect against pulsed lasers.¹⁹⁵ (A similar device using microdroplets of liquid crystals and depending on the optical Kerr effect has also been reported.¹⁹⁶ The response time is on the order of 50 microseconds for this system.¹⁹⁶)

A device similar to the liquid crystal composite has been proposed that would use a dispersion of $\chi^{(3)}$ microparticles in a polymeric host (Fig. 29). The design principle is to make use of the intensity dependent refractive index, n_2 . At low light irradiances, the index matched particles and host will let the light pass through unaffected. However, at high irradiances, the index of refraction of the nonlinear optical material changes, creating an index mismatch and thereby scattering the incoming light. The advantages to this type of device are that it is passive, i.e., powered by the light itself, it is fast enough to protect against pulsed laser threats if electronic polarizable $\chi^{(3)}$ materials (see Table 4) are used and that the device is normally optically transparent.

Another $\chi^{(3)}$ material device concept, based on four wave mixing, is diagrammed in Fig. 30. In this type of device, two counterpropagating lasers (beams 1 and 2) setup a phase grating in the nonlinear optical material that rejects a high intensity input laser beam (beam 3) while letting a low intensity input beam pass through unaffected. These counterpropagating beams can be at the same frequency as the input beam (degenerate four wave mixing) or at a different frequency (nondegenerate four wave mixing). Most device designs employ a permanent set of crossed laser beams, but using a beam splitter as diagrammed, the incident beam can be used to form these beams. The rejected beam (beam 4) is conjugate to the input beam which is why this method is sometimes referred to as phase conjugation. (By phase conjugation, we mean that the rejected beam has the same phase as the input beam but travels in exactly the

KERR CELL

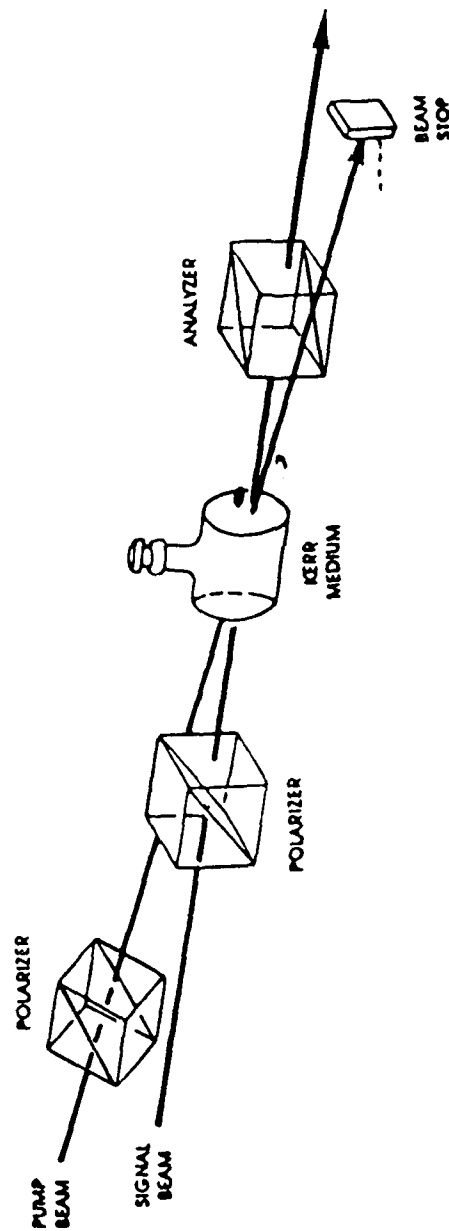


Figure 28: The Optical Kerr Effect Device uses optical electric-field induced birefringence. The basic optical train remains the same as in the Linear Electro-Optic Device.

POWER LIMITER: X^3 COMPOSITE

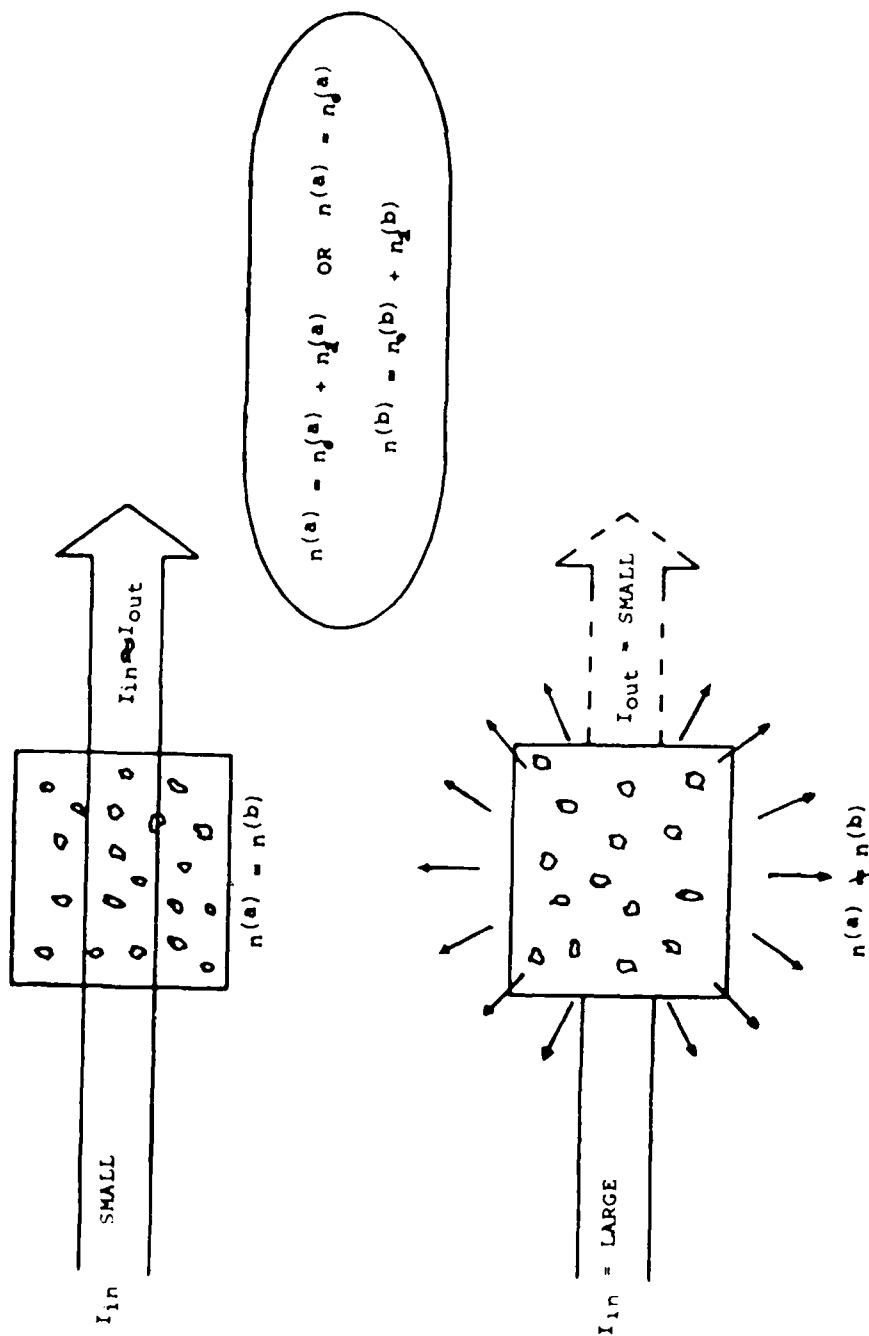


Figure 29: Diagrammed is a power limiter device concept based on third order materials. At low input intensity, the light passes through virtually unaffected. However, at high intensity a refractive index mismatch is formed via n_2 and the input beam is scattered. In this type of device only one material must be optically nonlinear.

FOUR WAVE MIXING DEVICES

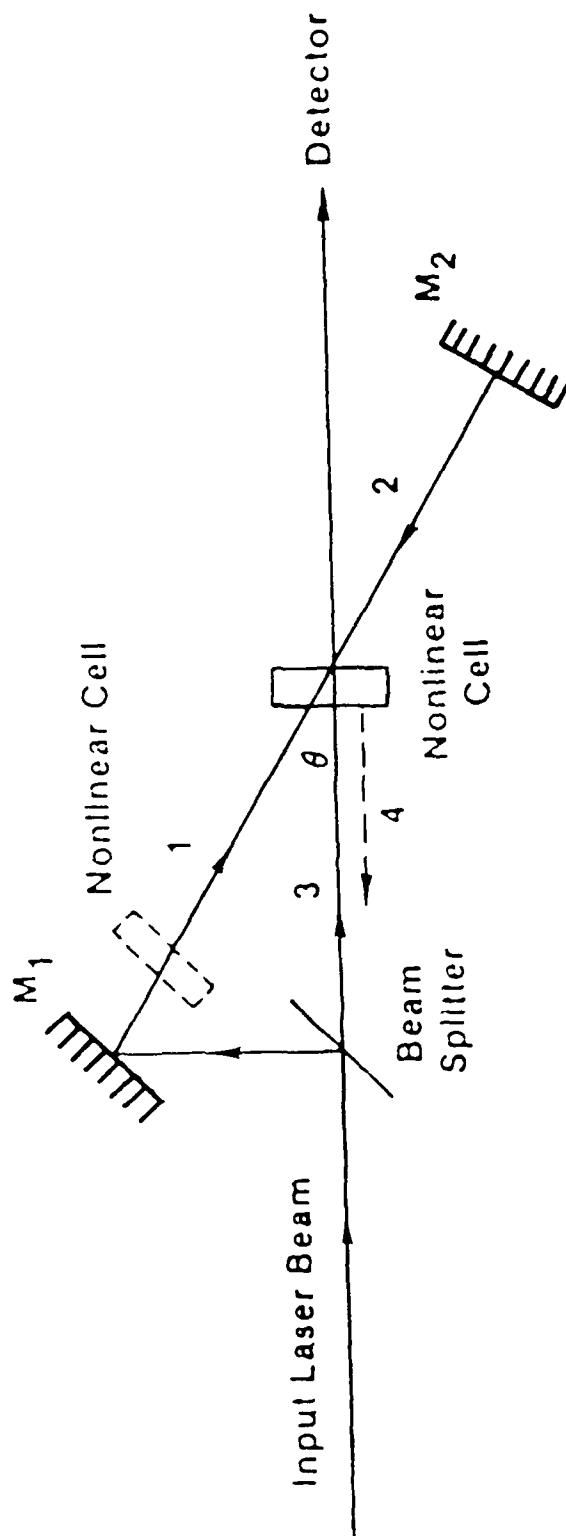


Figure 30: A schematic diagram of a four wave mixing device where the input beam (3) is used to form the pump beams (1 and 2). See the text for a more detailed description of the device operation.

opposite direction, a sort of time reversal symmetry. See Fig. 31.)^{28,161} This device requires the use of electronic $\chi^{(3)}$ materials (Table 4) to protect against pulsed lasers.

Another grating type device suggested for use in eye/sensor protection uses photorefractive materials.¹⁶² In these materials, a weak probe beam and a strong incident beam are crossed setting up an intensity distribution which in turn results in a space charge density distribution as diagrammed in Fig. 32. The resulting space charge electric field and index modulation are out of phase with respect to the intensity distribution resulting in a phase grating. This type of effect is limited by the ability of charges to migrate and define the space charge density.^{163,164} Literature reports suggest a fundamental response time limit on the order of picoseconds (10^{-12} sec).^{163,164} The only materials observed to exhibit this effect thus far are certain inorganic crystals. The possibility of such effects arising in organometallic and metal doped polymeric materials has been proposed.

One final device concept involves the intensity dependent refractive index, n_2 . In these beam bending devices, diagrammed in Fig. 33, high intensity light alters the refractive index of the nonlinear optical material, deflecting the beam out of the normal optical path. While such devices are simple in concept, they are difficult to put into practice. This is because a high intensity symmetric beam will experience a symmetric phase shift and so will not deflect out of the optic path.¹⁶⁵ A variety of methods for imparting an asymmetric profile to the input beam have been suggested, many making use of grating type structures as diagrammed in Fig. 33.

OPTICAL PHASE CONJUGATION

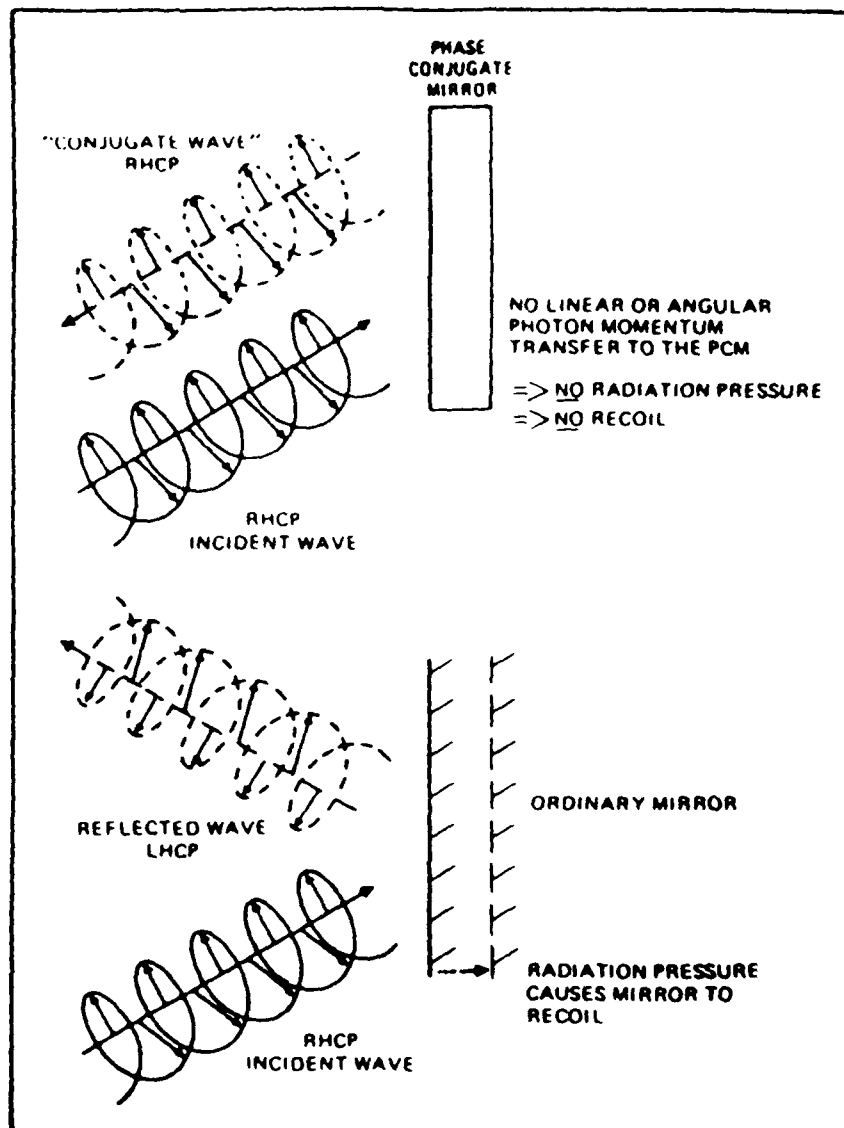


Figure 31: The concept of phase conjugation is illustrated using left and right handed circularly polarized light (LHCP and RHCP, respectively) and a phase conjugate (top of figure) and ordinary mirror (bottom of figure). This figure was adapted from Ref. 161.

PHOTOREFRACTIVE DEVICES

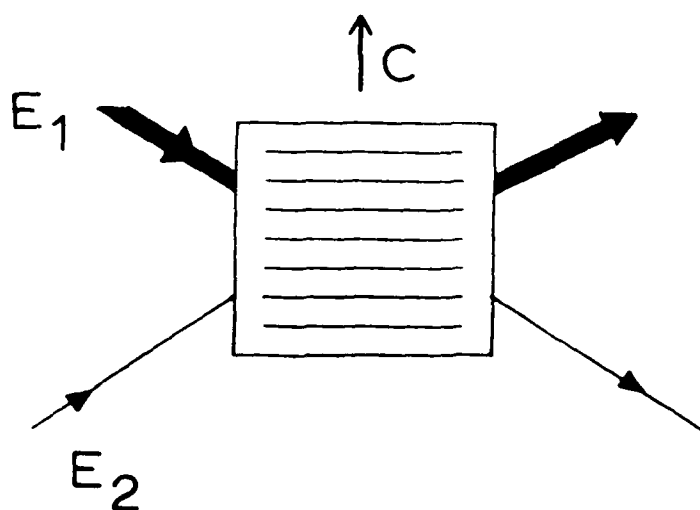
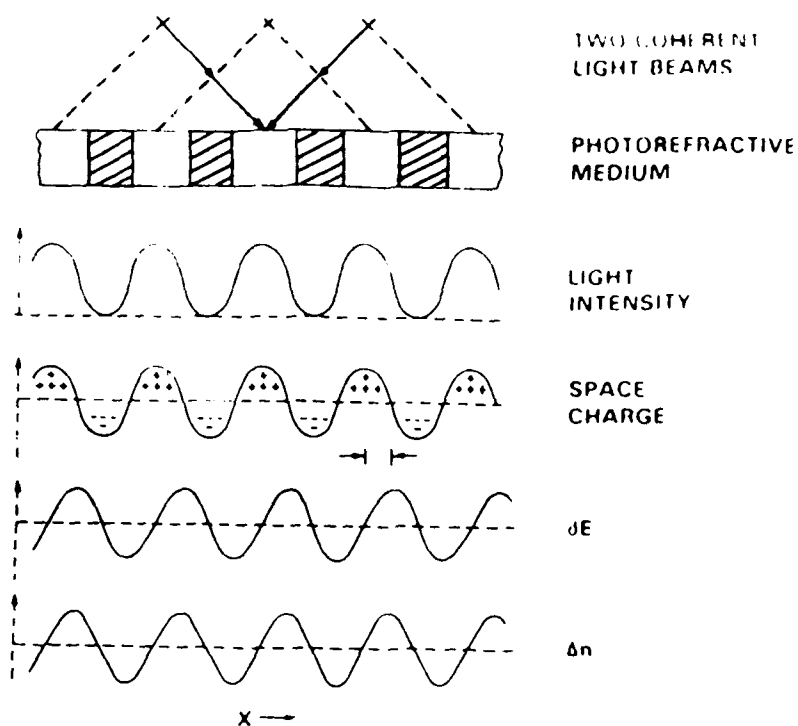


Figure 32: The upper half of the figure diagrams the evolution of the photorefractive material response. Diagrammed in the lower half of the figure is a configuration which could be used for eye/sensor protection. At low irradiance levels, E_1 would continue unhindered through the crystal. However, at high irradiances, E_1 would be deflected out of the optical path.

eye damage thresholds, W_e :¹

* For pulse durations of 1 - 18 ns: $W_e = 0.5 \mu\text{J}/\text{cm}^2$

* For longer pulse durations, up to 10 sec.s:

$$W_e = 1.8 t^{3/4} \text{ mJ}/\text{cm}^2 \quad (t \text{ in seconds})$$

As an example, using the forementioned damage thresholds and a value of $100 \text{ mW}/\text{cm}^2$ for the output of the sun,² an eye protection device must attenuate the light by a factor equivalent to 1.5 optical density units (ODU) (a transmission reduction of 97%) when directed at the sun.

PROTECTION STRATEGIES

Any successful eye/sensor protection device must interact with and attenuate the laser light before it reaches the detector system. The interaction of light with matter is usually classified in one of three categories: absorption, dispersion or scattering. Absorption can be an effective protection strategy and representative examples of absorption devices under investigation include particle suspension, chalcogenide, VO_2 , Ge, and two-photon absorption activated power limiters. However, such devices often have reduced transparency in the visible spectral region or unacceptable response times. Therefore, much of the recent research into eye/sensor protection has focussed on using dispersion or scattering to redirect the light and this is where nonlinear optical materials have the greatest potential for impact in the near term: nonlinear optical materials can have unique index of refraction properties and fast response times.

ORGANIC NONLINEAR OPTICAL MATERIALS

Nonlinear optical materials have been known and studied for over two decades with most research efforts being successfully directed at inorganic materials,^{5,25,26} in particular, inorganic crystals²⁷, glasses^{28,29} and semiconductors.³⁰⁻³² The most familiar example of inorganic nonlinear optical materials are crystals such as potassium dihydrogen phosphate (KDP) and lithium niobate (LiNbO_3). However, more recently, interest has focussed on such inorganic materials as tungsten bronze crystals.³³ With the recent emphasis on optical computing and communication, a need for nonlinear optical materials with better mechanical processing and physical properties than available in typical inorganic nonlinear optical materials has become apparent and researchers have turned to examine organic polymeric materials.^{9,14,17-21,34-39} It is now generally agreed that organic materials have the potential for nonlinear optical effects which are orders of magnitude better than currently used inorganic materials.^{5,6,12,14,17-21,34,37,38,40-45} This is based on the origin of the nonlinear optical effect in organic materials: the easily polarized molecular electric fields.^{7,10,14,15} Extensive research is underway on the development of nonlinear optical organic materials and a

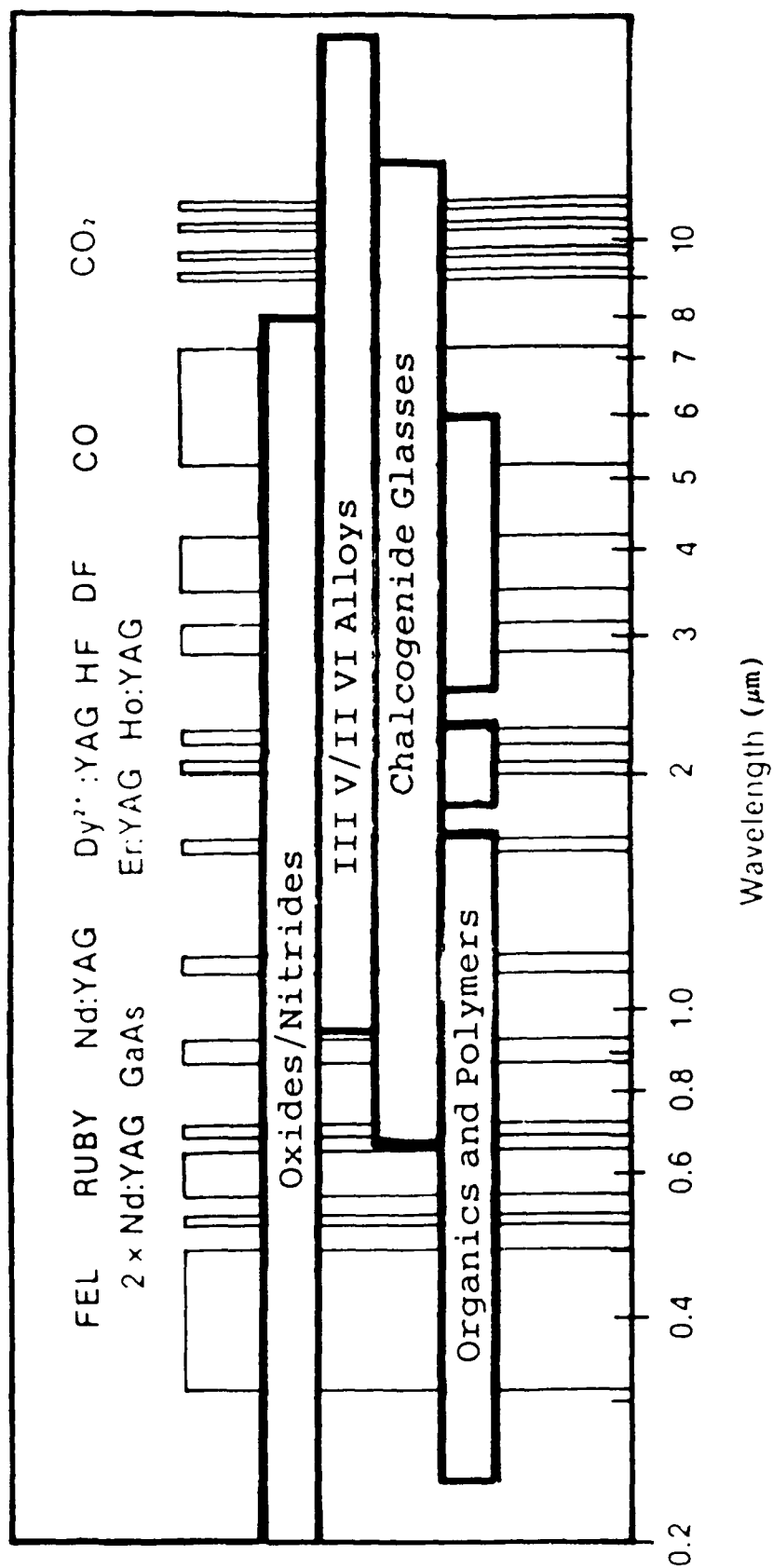


Figure 6: A graphic representation of various lasers available in modern laboratories and the spectral transmission windows of potential laser hardening materials.

BEAM BENDING DEVICES

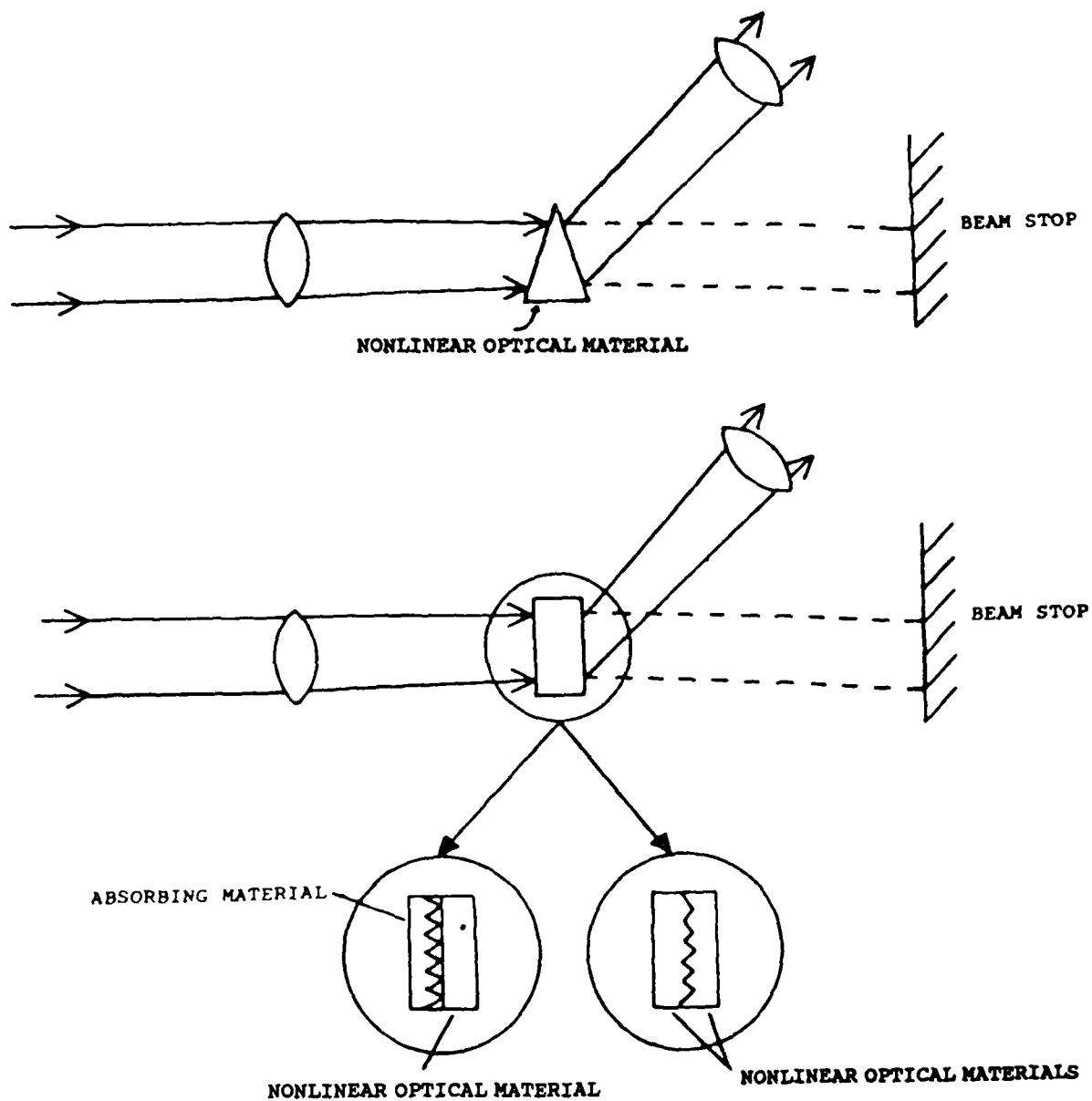


Figure 33: An illustration of the beam bending device concept.

PROPOSED FUTURE RESEARCH EFFORTS

In reviewing research efforts to develop organic nonlinear optical materials for eye/sensor protection, several novel ideas have surfaced which the authors would like to propose.

The first idea involves using stretched copolymer films to assist in enhancing nonlinear optical effects in materials. Although extensive work has been reported on copolymer systems, polymer film alignment by stretching^{13, 36} has not received much attention. The technology for stretching films is well developed; this is the way Polaroid filters and lenses are prepared. The following figure (Fig. 34) is a schematic diagram of how the process would help to increase molecular order in the material and thereby increase the magnitude of the nonlinear optical effect.

Another idea that has been proposed by other researchers and which may have great potential, is organic superlattices. In general, organic superlattices can be envisioned as structures with an alternating composition on a molecular scale. This alternating composition is repeated in only one direction so that the electrons are confined along a chain.⁴ The following diagrams (Fig. 35 and 36) indicate how these organic systems would imitate the more familiar semiconductor superlattices, and give an idea of the type of control that may be available via substituent groups.

Production of these types of materials via copolymer synthesis and Langmuir-Blodgett film deposition has been suggested. These are both areas of established expertise in the Polymeric Materials Branch at NRL.

Finally, little information was uncovered concerning investigations into the potential of inorganic polymer systems for use in eye and sensor protection. Inorganic polymers, such as the linear polyphosphazenes and polythiazyl (Fig. 37), can exhibit extensive conjugation, a necessary condition for enhanced nonlinear optical behavior, and enhanced ancillary properties. For example, silicon based polymer systems should have enhanced thermal damage thresholds. Additional theoretical and experimental investigations into the potential of polymer systems like those described above should be considered.

ACKNOWLEDGMENTS

One of us (MEB) was an ONT Postdoctoral Fellow during part of this work and would like to thank both the Office of Naval Technology and the American Society for Engineering Education. We would also like to thank Dr. Filbert J. Bartoli Jr., Optical Sciences Division, Naval Research Laboratory for his helpful discussions and comments.

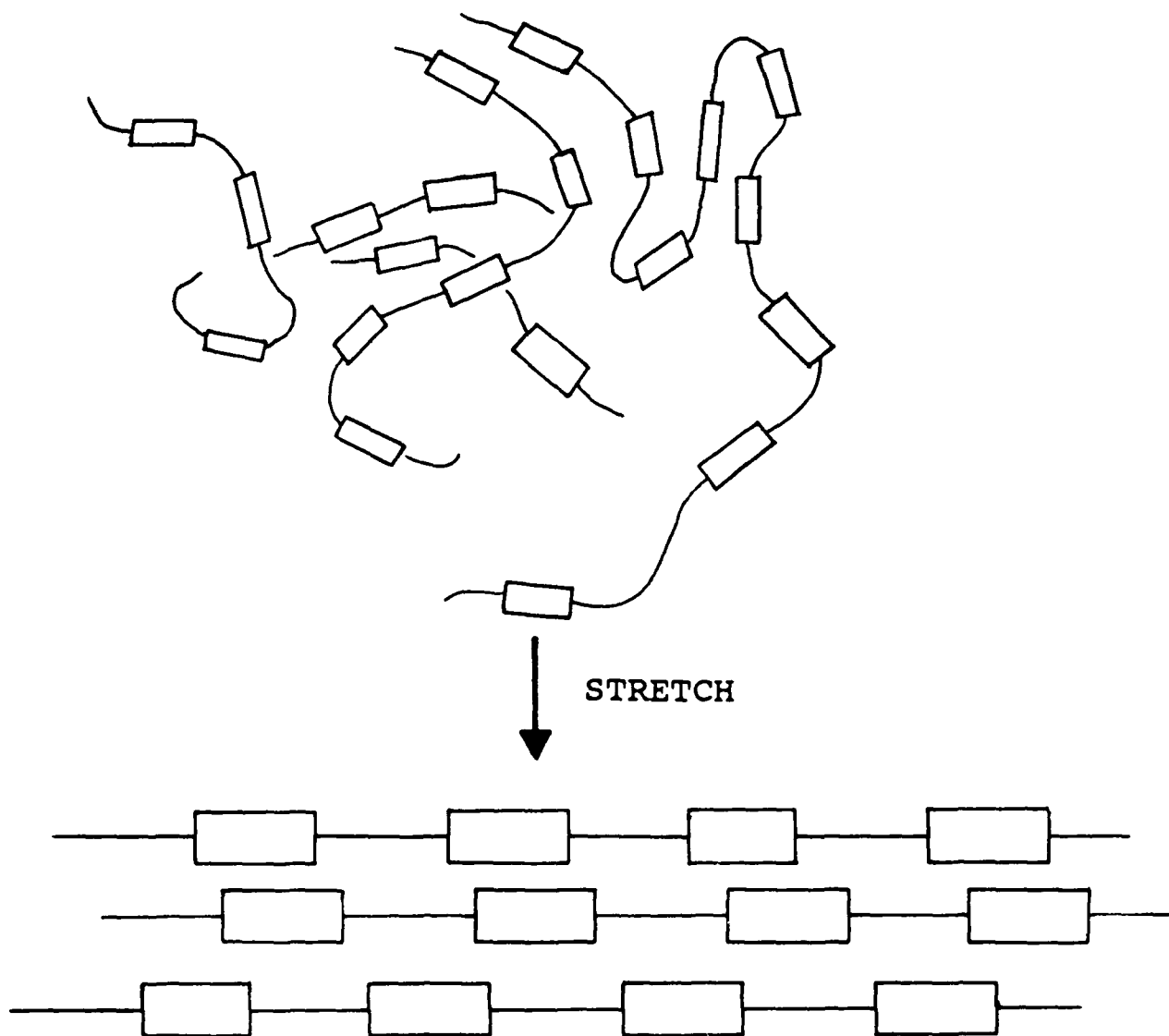


Figure 34: The enhancement in the molecular packing, and thus the nonlinear optical effect, of a copolymer film via stretching is diagramed. The rectangles represent the nonlinear optical units or blocks in the copolymer.

ORGANIC SUPERLATTICES

ORDERED STRUCTURES

LANGMUIR-BLODGETT FILMS	ALTERNATE COPOLYMERS	BLOCK COPOLYMERS
$\begin{array}{l} \text{-B-B-B-B-B-B-B-B-B-B-} \\ \text{-A-A-A-A-A-A-A-A-A-A-} \\ \text{-B-B-B-B-B-B-B-B-B-B-} \\ \text{-A-A-A-A-A-A-A-A-A-A-} \end{array}$	$[-\text{A-B-A-B-A-B-A-B-A-}]_n$	$[-\text{A-A-A-B-B-B-A-A-A-B-B-B-}]_n$

Figure 35: Schematic diagrams of possible organic superlattice structures. The As and Bs represent different types of monomers, the basic building blocks of polymers.

ORGANIC SUPERLATTICES

BLOCK COPOLYMERS

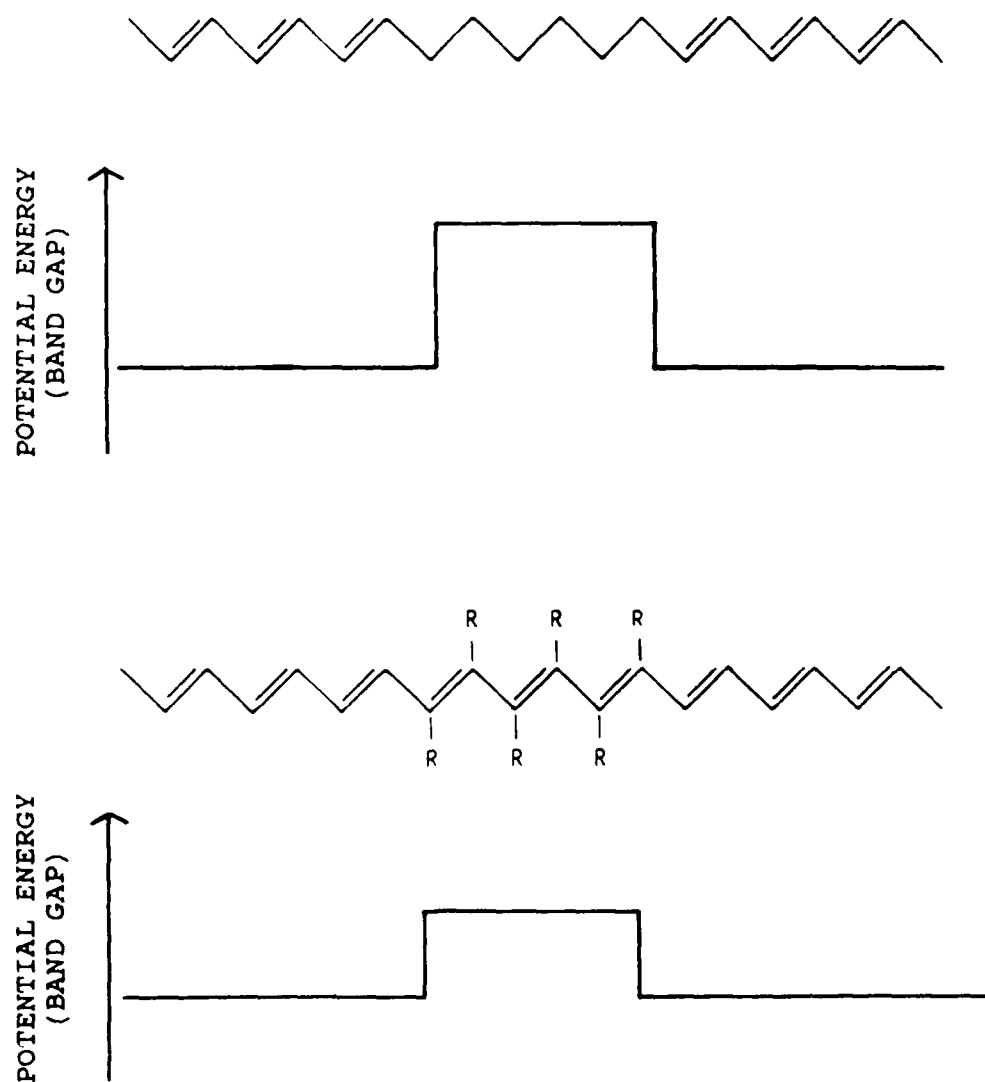


Figure 36: An example of how the properties of organic superlattices, using block copolymers, might be modified for specific applications.

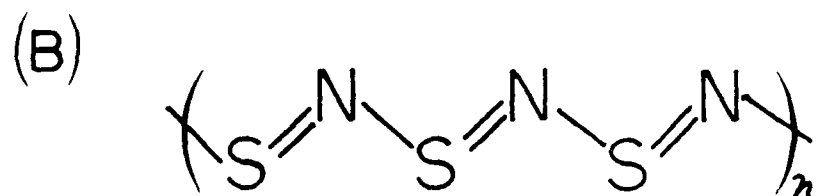
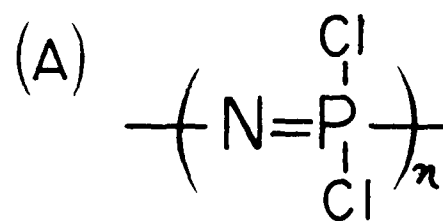


Figure 37: Two inorganic polymers (a) linear polyphosphazene and (b) polythiazyl demonstrating extensive π conjugation, a requirement for nonlinear optical behavior, are shown.

APPENDIX A: LISTING OF χ^3 MATERIALS

THE FOLLOWING LIST OF ORGANIC AND INORGANIC χ^3 MATERIALS IS NOT AN EXHAUSTIVE COMPILATION OF REPORTED RESULTS. RATHER, IT IS AN ATTEMPT TO DEMONSTRATE THE WIDE VARIETY OF MATERIALS THAT HAVE OR ARE BEING EXAMINED AND THE MAGNITUDE OF THEIR RESPECTIVE NONLINEAR OPTICAL EFFECTS.

THE FOLLOWING ABBREVIATIONS ARE USED FOR MATERIAL NAMES:

PMMA	POLY(METHYL METHACRYLATE)
MBBA	N-(P-METHOXYBENYLIDENE)-P-BUTYLANILINE
PBT	POLY(P-PHENYLENEBENZOBISTHIAZOLE)
4-BCHU	4-BUTOXYCARBONYLMETHYLURETHANE
PTS	POLY(BIS(P-TOLUENE SULFONATE))
DMA-NS	PARADIMETHYLAMINO-B-NITROSTYRENE
DMA-PND	PARADIMETHYLAMINO-L PHENYL, 4-NITROBUTADIENE
PC	PTHALOCYANINE
MNA	METHYLMITROANILINE
DMSO	DIMETHYLSULFOXIDE
PPV	POLY(P-PHENYLENE VINYLENE)
TCMQ	TETRACYANOQUINODIMETHANE
PDA	POLYDIACETYLENE
PBO	POLY(P-PHENYLENE-2, -6 BENZOBISOXAZOLE)
PDIAB	POLY(P-PHENYLENE BENZOFISDIAZOLE)
PBI	POLY(BENZIMIDAZOLE)
BBB	POLY(6,9-DIHYDRO-6,9-DIOXOBISBENZIMIDAZO(2,1-B:1',2'-J)BENZO(LMN)PHENANTHROLINE-2,11-DIYL)
BBL	POLY[(7-OXO-7,10-BENZ[DE]IMIDAZO(4',5':5,6)-BENZIMIDAZO(2,1-A)ISOUINOLONE-3,4:10,11-TETRAYL)-10-CARBONYL]
POL	POLY[1,6-DIHYDROPYRAZINE(2,3-C)-QUINOXALINE-2,3,8-TRIYL-7(2H)-YLIDENE-7,8-DIMETHYLIDENE]
POL	POLY(2H,11H-BIS[1,4]OXAZINO[3,2-B:3'2'-N]TRIPHENODIOXAZINE-3,12-DIYL-2,11-DIYLIDENE-11,12-BIS(METHYLIDENE))
FTL	POLY(2H,11H-BIS[1,4]TRIAZINO[3,2-B:3',2'-N]TRIPHENODITHIAZINE-3,12-DIYL-2,11-DIYLIDENE-11,12-BIS(METHYLIDENE))
DFMP	POLY(2,5-BIS(TRIFLUOROMETHYL)PHENYLDIACETYLENE)
BTTP	POLY(4-BUTYL-2,3,5,6-TETRAFLUOROPHENYLDIACETYLENE)

THE FOLLOWING ABBREVIATIONS ARE USED IN DESCRIBING THE MATERIAL/MOLECULAR FORM:

TF	THIN FILM
LB	LANGMUIR/BLODGETT FILM
SOLN	SOLUTION
LIQU	LIQUID
MLTN	MOLTEN
LC	LIQUID CRYSTAL
CRYS	CRYSTAL
PLAT	CRYSTAL PLATLETS
MONO	MONOMER
POLY	POLYMER

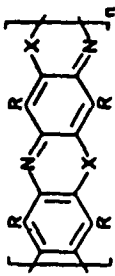
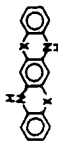


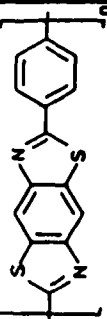
THE FOLLOWING ABBREVIATIONS ARE USED IN DESCRIBING THE EXPERIMENTAL METHOD FOR DETERMINING THE NONLINEAR OPTICAL EFFECT:

DFWM	DEGENERATE FOUR WAVE MIXING
THG	THIRD HARMONIC GENERATION
RWG	REFLECTION WAVEGUIDE
OKE	OPTICAL KERR EFFECT
EFISH	ELECTRIC FIELD INDUCED SECOND HARMONIC GENERATION
SATIN	SATURATION INTENSITY
SP	SURFACE PLASMON
ETAL	NONLINEAR ETALON EXPERIMENT

NOTES

- (1) IN THE COLUMN DESCRIBING THE MAGNITUDE OF THE χ^3 EFFECT, QUANTITIES ENCLOSED IN PARENTHESSES ARE MOLECULAR HYPERPOLARIZABILITIES, γ . UNLESS OTHERWISE INDICATED, THE REPORTED VALUE IS AN EXPERIMENTAL MEASUREMENT.
- (2) THE COLUMN LABELED TIME REFERS TO THE RESPONSE TIME OF THE NONLINEAR OPTICAL MATERIAL.
- (3) DATA OBTAINED FROM NON-REFEREED SOURCES SUCH AS ORAL PRESENTATIONS AND CONFERENCE LECTURE NOTES ARE INDICATED IN THE REFERENCE COLUMN USING A SUPERScript *.

CLASS: BOND ALTERNATION (LADDER AND RIGID ROD)

MOLECULE/MATERIAL		NONLINEAR OPTICAL EFFECT					REFERENCES				
NAME	STRUCTURE	FORM	χ^3 or (γ) (esu)	n_2 (cm^2/W)	λ (μm)	Res/NonRes	TIME	METHOD	AUTHOR	REF#	YEAR
PXL											
PQL	X=NH; R=H R=[CH=CHN(CH ₂ CH ₃) ₂]; PREPARATION A R=[CH=CHN(CH ₂ CH ₃) ₂]; PREPARATION B	TF	3E-10 2.8E-9 5E-11		0.53	R	ps	DFWM	DALTON [†] DALTON [†] DALTON [†]	80 80 193	1988 1988 1988
	R=[CH=CHN(CH ₂ CH ₂ CH ₃) ₂] R=[CH=CHNC ₃ H ₇] R=[CH=CHNC ₆ H ₁₃]	TF	2.8E-10 1.3E-9 7E-10 1.1E-9		0.53	R	ps	DFWM	DALTON [†] DALTON [†] DALTON [†]	80 193 80	1988 1988 1988
PXL	X=CH; PRISTINE 		5E-10						ULRICH [†] DALTON [†]	37 80	1988 1988
PXL	X=CH; BIPOLARON 		1E-7						ULRICH [†] DALTON [†]	37 80	1988 1988
PXL	X=CH; PROTONATED 		2E-13						ULRICH [†] DALTON [†]	37 80	1988 1988
PBT		TF	50-100E-12 9E-12 1E-10	5E-7	1.90 0.58±0.60	NR NR	<ps	THG DFWM	GARITO RAO ULRICH [†] DOMASH [†]	10 13 37 187	1986 1986 1988 1988

CALCULATED

CLASS: BOND ALTERNATING (LADDER AND RIGID ROD)

NAME	MOLECULE/MATERIAL STRUCTURE	FORM	NONLINEAR OPTICAL EFFECT					REFERENCES			
			χ^3 or (γ) (esu)	n_2 (cm^2/MW)	λ (μm)	Res/NonRes	TIME	METHOD	AUTHOR	REF#	YEAR
PBO			2.5E-11		0.63	NR		DFWM	PRASAD [†]	81	1988
PDIAB											
PBI		TF TF	8E-13 7E-13		1.90 1.90	NR NR		THG THG	GARITO [†] STAMANOFF [†]	10 96	1986 1988
BBL		TF TF	2E-9 7E-11 ~E-10		0.53 1.06	NEAR R R NEAR R		ps ps	DALTON [†] DALTON KAFABI [†]	80 193 197	1988 1988 1989
BBB		TF	~E-11		1.06	NR		ps	KAFABI [†]	197	1989

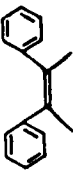
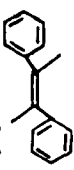
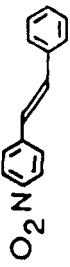

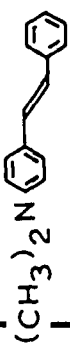
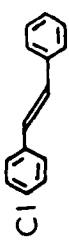

CLASS: LONG CHAIN UNSATURATED

MOLECULE/MATERIAL		NONLINEAR OPTICAL EFFECT					REFERENCES				
NAME	STRUCTURE	FORM	χ^3 or (γ) (esu)	n_2 (cm ² /W)	λ (μ m)	Res/NonRes	TIME	METHOD	AUTHOR	REF#	YEAR
POLYDIACETYLENE											
PDA-PTS:	$R=R'=\text{CH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3$	TF	9E-9	3E-6	0.70	NR	1ps	DFWM	CARTER	122	1985
		PLAT	5E-10		0.65	R	<6p	DFWM	CARTER	133	1985
		CRYST	1.6E-10	1.8E-6	0.70	NR	<6ps	DFWM	CARTER	133	1985
		CRYST	8.5E-10		2.62	NR		THG	SAUTERET	125	1976
		CRYST	3E-9		1.89	R		THG	SAUTERET	125	1976
		TF		1E-6	1.9	NR		ETAL	HERMANN	180	1980
		TF	1.1E-11		>0.70	NR	<3ps	RWG	CARTER	136	1984
		COMPOSITE/PMMA	1E-9		1.94	R		DFWM	NAKANISHI	131	1988
									PRASAD*	82	1988
PDA-TCDDU:	$R=R'=(\text{CH}_2)_4\text{OCONHC}_6\text{H}_5$	PLAT		1E-6	>0.70	NR		RWG	CARTER	136	1984
		MONO	1.2E-13		1.89	near R		THG	SAUTERET	125	1976
		POLY	7.5E-11		1.89	near R		THG	SAUTERET	125	1976
		POLY	3.7E-11		2.62	NR		THG	SAUTERET	125	1976
PDA-4BCMU:	$R=R'=(\text{CH}_2)_4\text{CCONHCH}_2\text{COOC}_6\text{H}_9$	TF RED	4E-10	1E-6	0.58 & 0.61	R(?)	<ps	DFWM	RAO	16	1986
		TF YLM	2.5E-11		0.58 & 0.61	R(?)	<ps	DFWM	RAO	16	1986
		COMPOSITE/PMMA	3E-10		0.53	R	10ps	OKE	HO	137	1987
		COMPOSITE/PMMA	3E-9		1.06	NR	<ps	OKE	HO	137	1987
POLY-DFMP:		(1.09 μ)TF	2.4E-11		1.83				NAKANISHI*	131	1988
		(0.98 μ)TF	3.7E-11		1.83				NAKANISHI*	131	1988
		(1.09 μ)TF	2.6E-11		1.94				NAKANISHI*	131	1988
		(0.98 μ)TF	2.4E-11		1.94				NAKANISHI*	131	1988
		(1.09 μ)TF	3.5E-11		1.88				NAKANISHI*	131	1988
POLY-BTFP:		(0.07 μ)TF	2.8E-10		1.83				NAKANISHI*	131	1988
		(0.05 μ)TF	2.6E-10		1.83				NAKANISHI*	131	1988
		(0.07 μ)TF	1.3E-10		1.94				NAKANISHI*	131	1988
		(0.05 μ)TF	1.5E-10		1.94				NAKANISHI*	131	1988
		(0.07 μ)TF	3.2E-10		1.88				NAKANISHI*	131	1988

CLASS: LONG CHAIN UNSATURATED

NAME	MOLECULE/MATERIAL	STRUCTURE	NONLINEAR OPTICAL EFFECT					REFERENCES				
			FORM	χ^3 or (γ) (esu)	n_2 (cm ² /MW)	λ (μ m)	Res/NonRes	TIME	METHOD	AUTHOR	REF#	YEAR
PDA		$R=CH_3(CH_2)_{15}$ $R'=(CH_2)_8COOH$	LB		1E-4	0.67-0.70	R		SP	CARTER	111	1985
			LB		1E-6	0.70-1.04	NR		SP	CARTER	111	1985
			CRYS									
PPV		$R=CH_3(CH_2)_{15}$ $R'=(CH_2)_8COOCd$	LB RED	3.4E-11	1E-10	1.064	R		THG	KAJZAR	34	1987
			LB RED	1.5E-10		1.35	R		THG	KAJZAR	34	1987
			LB RED	2.2E-10		1.907	R		THG	KAJZAR	34	1987
			LB BLU	9E-12		1.064	R		THG	KAJZAR	34	1987
			LB BLU	1.9E-11		1.35	R		THG	KAJZAR	34	1987
			LB BLU	3.4E-11		1.907	R		THG	KAJZAR	34	1987
			TRANS	4E-11		1.064	R		THG	KAJZAR	34	1987
			TRANS	1.2E-9		1.35	R		THG	KAJZAR	34	1987
			TRANS	1.3E-9		1.907	R		THG	KAJZAR	34	1987
			TF	1E-10	5E-7	0.60		ps	DFWM	KARASZ [†]	188	1988
H ₂ PC NiPC CuPC PbPC PtPC			LB	3E-9		0.60	R	ps	DFWM	PRASAD	190	1988
			LB	~1E-9		0.60	R	ps	DFWM	PRASAD	190	1988
			LB	~1E-9		0.60	R	ps	DFWM	PRASAD	190	1988
			CHCl ₃ SOLN	3E-11		1.06	NR	ps	DFWM	SHIRK [†]	198	1989
			CHCl ₃ SOLN	2E-11		1.06	NR	ps	DFWM	SHIRK [†]	198	1989
Polythiophene			TF&LB	1E-9		0.60	R	ps	DFWM	PRASAD [†]	82	1988
TCNQ			LB	5E-12		1.39	R		THG	EGBERT [†]	189	1988

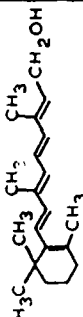
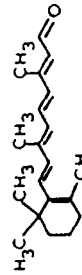
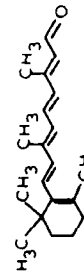

CLASS: LONG CHAIN UNSATURATED

MOLECULE/MATERIAL		NONLINEAR OPTICAL EFFECT						REFERENCES			
NAME	STRUCTURE	FORM	χ^3 or (γ) (esu)	n_2 (cm^2/MW)	λ (μm)	Res/NonRes	TIME	METHOD	AUTHOR	REF#	YEAR
cis-STILBENE		LIQU	(1.7E-35)		1.06				OU DAR	75	1977
trans-STILBENE/ C_6H_6		SOLN	(4.8E-35)		1.06				OU DAR	75	1977
4-NITROSTILBENE/ C_6H_6		SOLN	(7.5E-34)		1.06				OU DAR	75	1977
4-AMINOSTILBENE/ C_6H_6		SOLN	(2E-34)		1.06				OU DAR	75	1977
4-DIMETHYLAMINOSTILBENE/ C_6H_6		SOLN	(4.7E-34)		1.06				OU DAR	75	1977
4-CHLOROSTILBENE/ C_6H_6		SOLN	(2.7E-35)		1.06				OU DAR	75	1977
4-CHLORO-4'-NITROSTILBENE/ CHCl_3		SOLN	(6.9E-34)		1.06				OU DAR	75	1977

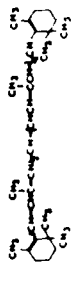
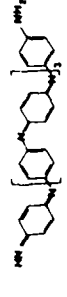
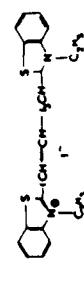
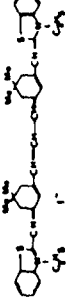
CLASS: LONG CHAIN UNSATURATED

MOLECULE/MATERIAL		NONLINEAR OPTICAL EFFECT					REFERENCES					
NAME	STRUCTURE	FORM	χ^3 or (γ) (esu)	n_2 (cm ² /MW)	λ (μm)	Res/NonRes	TIME	METHOD	AUTHOR	REF#	YEAR	
4-CHLORO-4'-DIMETHYLAMINOSTILBENE/CHCl ₃ SOLN		SOLN	(1E-33)		1.06				EFISH	UDAR	75	1977
4-NITRO-4'-AMINOSTILBENE/CH ₂ Cl ₂ SOLN		SOLN	(9.9E-33)		1.06				EFISH	UDAR	75	1977
4-NITRO-4'-DIMETHYLAMINOSTILBENE/CH ₂ Cl ₂ SOLN		SOLN	(1.7E-32)		1.06				EFISH	UDAR	75	1977
DMA-NS/CHCl ₃		SOLN	(8.8E-32)		1.06				EFISH	UDAR	75	1977
DMA-PNB/CH ₂ Cl ₂		SOLN	(2.8E-32)		1.06				EFISH	UDAR	75	1977
NEMATIC MBBA CH ₃ OC ₆ H ₄ CHNC ₆ H ₄ (CH ₂) ₃ CH ₃		LC	6E-13(z) 3E-14(x)		1.91 1.91 0.69		μs		THG THG DFWM	WONG WONG FEXETE	153 153 159	1986 1986 1980
ISOTROPIC MBBA CH ₃ OC ₆ H ₄ CHNC ₆ H ₄ (CH ₂) ₃ CH ₃		LC	3E-13		1.91				THG	WONG	153	1986

CLASS: LONG CHAIN UNSATURATED

MOLECULE/MATERIAL		NONLINEAR OPTICAL EFFECT					REFERENCES				
NAME	STRUCTURE	FORM	χ^3 or (γ) (esu)	n_2 (cm^2/MW)	λ (μm)	Res/NonRes	TIME	METHOD	AUTHOR	REF#	YEAR
RETINOL		MLTN	5.0E-13 (4.6E-35)		1.89 1.89				THG THG	86 86	1974 1974
RETINAL		MLTN	1.1E-12 (9E-35)		1.89 1.89				THG THG	86 86	1974 1974
trans-RETINAL/DMSO (10E20 molecules/ cm^3)		SOLN	(1.3E-34)		1.89				THG	86	1974
cis-trans BIXINE/DMSO (10E20 molecules/ cm^3)		SOLN	(3E-34)		1.89				THG	86	1974
DODECAPRENO- β -ETA-CAROTENE/ C_6H_6 (10E18 molecules/ cm^3)		SOLN SOLN	(1.7E-32) (4E-33)		1.89 2.47				THG THG	86 86	1974 1974

CLASS: LONG CHAIN UNSATURATED

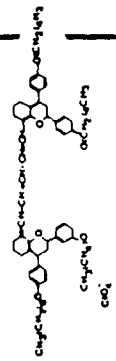
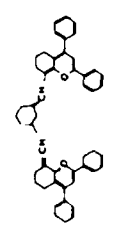
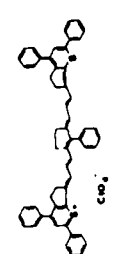
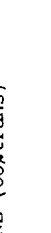
MOLECULE/MATERIAL		NONLINEAR OPTICAL EFFECT					REFERENCES				
NAME	STRUCTURE	FORM	χ^3 or (γ) (esu)	n_2 (cm^2/MW)	λ (μm)	Res/NonRes	TIME	METHOD	AUTHOR	REF#	YEAR
BETA-CAROTENE											
	(10E19/ cm^3) / C_6H_6	GLASS	1E-12	8.1E-8*	1.89	NR		THG	HERMANN	87	1973
	(10E19/ cm^3) / C_6H_6	SOLN	(1.4E-33)		1.89			THG	HERMANN	86	1974
	/ETHANOL	SOLN	(1.1E-33)		2.47	R		THG	HERMANN	86	1974
	/ETHANOL	SOLN	1.4E-13**		1.064	R		DFWM	MALONEY	83	1987
	/ETHANOL	SOLN	(7.6E-31)***		1.064	R		DFWM	MALONEY	83	1987
NIGROSINE/WATER											
		SOLN	1.9E-12**		1.064	R		DFWM	MALONEY	83	1987
			(5.2E-30)***		1.064	R		DFWM	MALONEY	83	1987
DTTC/METHANOL											
		SOLN	5.7E-13**		1.064	R		DFWM	MALONEY	83	1987
			(3.5E-29)***		1.064	R		DFWM	MALONEY	83	1987
DNTPC/METHANOL											
		SOLN	7.3E-13**		1.064	R		DFWM	MALONEY	83	1987
			(2.3E-29)***		1.064	R		DFWM	MALONEY	83	1987

* CONVERTED FROM esu TO cm^2/MW USING: 1 esu = $8.1 \times 10^3 \text{ cm}^2/\text{MW}$.¹²⁷

** CONVERTED FROM MKS(m^2/V^2) TO esu USING: $10^{-14} \text{ esu} = 1.4 \times 10^{-22} \text{ MKS}$.⁵²

*** CONVERTED FROM MKS(m^5/V^2) TO esu USING $\gamma_{esu} = \gamma_{SI} \times 7.16 \times 10^{13}$.⁸³

CLASS: LONG CHAIN UNSATURATED

MOLECULE/MATERIAL		NONLINEAR OPTICAL EFFECT					REFERENCES				
NAME	STRUCTURE	FORM	χ^3 or γ (esu)	n_2 (cm ² /W)	λ (μm)	Res/NonRes	TIME	METHOD	AUTHOR	REF#	YEAR
A9860/1,2 DICHLOROETHANE		SOLN	1.3E-12* (1.9E-28)**		1.064 1.064	R R		DFWM DFWM	MALONEY MALONEY	83 83	1987 1987
IR5/1,2 DICHLOROETHANE		SOLN	1.5E-12* (1.4E-28)**		1.064 1.064	R R		DFWM DFWM	MALONEY MALONEY	83 83	1987 1987
S501/1,2 DICHLOROETHANE		SOLN	8.9E-12* (9.1E-29)**		1.064 1.064	R R		DFWM DFWM	MALONEY MALONEY	83 83	1987 1987
BUTADIENE			(3.5E-36)		0.69			EFISH	GARITO [†]	78	1988
HEXATRIENE (60%trans)			(1.1E-35)		0.69			EFISH	GARITO [†]	78	1988
OCTATETRAENE (cis)			(1.8E-36)		0.65			EFISH	GARITO [†]	78	1988

* CONVERTED FROM MKS(m^2/V^2) TO esu USING: 10^{-14} esu $\approx 1.4 \times 10^{-22}$ MKS.⁵²

** CONVERTED FROM MKS(m^5/V^2) TO esu USING $\gamma_{\text{esu}} = \gamma_{\text{MKS}} \times 7.16 \times 10^{13}$.⁸³

CLASS: LONG CHAIN UNSATURATED

MOLECULE/MATERIAL		NONLINEAR OPTICAL EFFECT					REFERENCES				
NAME	STRUCTURE	FORM	χ^3 or (τ) (esu)	n_2 (cm ² /MW)	λ (μm)	Res/NonRes	TIME	METHOD	AUTHOR	REF#	YEAR
PCBS: A BIPHENYL, SIDE-CHAIN LIQUID CRYSTAL POLYMER; A PROPRIETARY PRODUCT OF HOECHST-CELANESE CORPORATION			2.4E-11*	5.0E-6*	0.53	NR	ns	DFWM	LIPSCOMB	47	1986
			.8E-13**	8.4E-7**	0.53	NR	ps	OKE	ALTMAN	116	1988
DVDA LIQUID CRYSTAL			4E-12	8.1E-7***				THG	GARITO	85	1985

* REPORTED AS $36 \times \text{CS}_2$. OBTAINED THE TABLE VALUE USING A VALUE OF $\chi^3 = 6.8\text{E}-13$ esu AND $n_2 = 1.4\text{E}-7 \text{ cm}^2/\text{MW}$ FOR CS_2 .¹⁸⁵

** REPORTED AS $6 \times \text{CS}_2$. OBTAINED THE TABLE VALUE USING A VALUE OF $\chi^3 = 6.8\text{E}-13$ esu AND $n_2 = 1.4\text{E}-7 \text{ cm}^2/\text{MW}$ FOR CS_2 .¹⁸⁵

*** CONVERTED FROM esu TO cm^2/MW USING: $1 \text{ esu} = 8.1 \times 10^3 \text{ cm}^2/\text{MW}$.¹²⁷



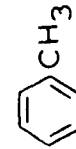
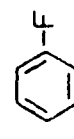
CLASS: ORGANOMETALLICS

MOLECULE/MATERIAL		NONLINEAR OPTICAL EFFECT						REFERENCES			
NAME	STRUCTURE	FORM	χ^3 or (γ) (esu)	n_2 (cm ² /MW)	λ (μ m)	Res/NonRes	TIME	METHOD	AUTHOR	REF#	YEAR
PALLADIUM POLY-YNE		TF	3.9E-11*	8.1E-6*	0.53	R			FRAZIER	143	1987
POLYSILANE		TF	1.5E-12 TOO SMALL		1.06 1.91	R NR			KAJZAR KAJZAR	145 145	1986 1986
BDN/TOLUENE		SOLN	1.2E-12** (6.2E-29)***		1.064 1.064	R R			MALONEY MALONEY	83 83	1987 1987

* REPORTED AS $58 \cdot n_2(CS_2)$. OBTAINED USING A VALUE OF $\chi^3 = 6.8E-13$ esu AND $n_2 = 1.4E-7$ cm²/MW FOR CS₂.¹⁸⁵

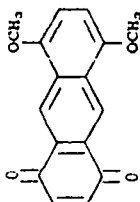
** CONVERTED FROM MKS(m²/V²) TO esu USING: 10^{-14} esu = 1.4×10^{-22} MKS.^{5,2}

*** CONVERTED FROM MKS(m⁵/V²) TO esu USING $\gamma_{esu} = \gamma_{SI} \times 7.16 \times 10^{13.83}$

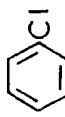
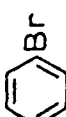

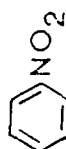
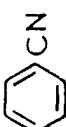
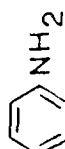

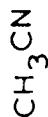
MOLECULE/MATERIAL		NONLINEAR OPTICAL EFFECT					REFERENCES				
NAME	STRUCTURE	FORM	χ^3 or (γ) (esu)	n_2 (cm ² /W)	λ (μ m)	Res/NonRes	TIME	METHOD	AUTHOR	REF#	YEAR
CdS/NAFION (perfluorosulfonic acid ion exchange film); 50 Å CdS particles		TF	NOT GIVEN		0.51	R	10 ns	DFWM	WANG	182	1987
MNA/PNMA: 17% MNA 10% MNA		TF TF	2.3E-12	2.5E-7	1.064 1.064			EFISH THG	GOODWIN KHANARIAN	11 175	1988 1986
AZO-DYE/COPOLYMER 25.9% DYE		TF	1.3E-12		2.050	NR		THG	MATSUMOTO	147	1987
$\left[\text{R} - \begin{array}{c} \text{CH}_2\text{CH} \\ \text{CH}_2\text{CH} \end{array} \begin{array}{c} \text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2 \\ \text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2 \end{array} \right]$ GOLD COLLOID: 100 Å DIAMETER SILVER COLLOID: 100 Å DIAMETER			1.5E-8 2.4E-9		0.527 0.527	R R	<5ps <5ps	DFWM DFWM	HACHE HACHE	146 146	1986 1986
POLYSTYRENE LATEX MICROSPHERES IN WATER (.234 MICRON DIAMETER)		SOLN	6.8E-8*	3.6E-3	0.514	NR		DFWM	SMITH	170	1981
BENZENE		LIQU LIQU LIQU LIQU	1.0E-13 (3.9E-36) 1.2E-13 1.1E-13		1.9 1.9 1.064 1.9	R R R R		THG THG THG THG	MEREDITH MEREDITH KAJZAR KAJZAR	115 115 34 34	1983 1983 1987 1987
TOLUENE		LIQU LIQU	9.8E-14 (4.6E-36)		1.9 1.9	R R		THG THG	MEREDITH MEREDITH	115 115	1983 1983
FLUOROBENZENE		LIQU LIQU	7.1E-14 (3.6E-36)		1.9 1.9	R R		THG THG	MEREDITH MEREDITH	115 115	1983 1983

* REPORTED AS $\sim 10^5 \times \text{CS}_2$. OBTAINED THE TABLE ENTRY USING $\chi^3 = 6.8 \times 10^{-13}$ esu FOR CS_2 .¹⁸⁵

CLASS: MISCELLANEOUS

MOLECULE/MATERIAL			NONLINEAR OPTICAL EFFECT					REFERENCES			
NAME	STRUCTURE	FORM	χ^3 or (γ) (esu)	n_2 (cm ² /W)	λ (μ m)	Res/NonRes	TIME	METHOD	AUTHOR	REF#	YEAR
POLYACENE QUINONE	in	TF	1.12E-11		0.53		ps	DFWM	BARBARA	192	1988
POLY(VINYL CHLORIDE)											
10% by weight											
											

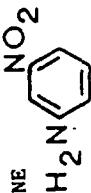
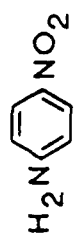
CLASS: MISCELLANEOUS

NAME	STRUCTURE	NONLINEAR OPTICAL EFFECT					REFERENCES				
		FORM	χ^3 or (γ) (esu)	n_2 (cm ² /W)	λ (μm)	Res/NonRes	TIME	METHOD	AUTHOR	REF#	YEAR
CHLOROBENZENE		LIQU LIQU	1.1E-13 (4.3E-36)		1.9 1.9	R R		THG THG	MEREDITH MEREDITH	115 115	1983 1983
BROMOBENZENE		LIQU LIQU	1.4E-13 (5.4E-36)		1.9 1.9	R R		THG THG	MEREDITH MEREDITH	115 115	1983 1983
IODOBENZENE		LIQU LIQU	2.4E-13 (8.2E-36)		1.9 1.9	R R		THG THG	MEREDITH MEREDITH	115 115	1983 1983
NITROBENZENE		LIQU LIQU LIQU LIQU	1.4E-13 (5.4E-36) 1.7E-13 (4.3E-35)		1.9 1.9 1.3 1.3	R R R R		THG THG EFISH EFISH	MEREDITH MEREDITH LEVINE LEVINE	115 115 54 54	1983 1983 1976 1976
CYANOBENZENE		LIQU LIQU	1.0E-13 (4.13E-36)		1.9 1.9	R R		THG THG	MEREDITH MEREDITH	115 115	1983 1983
ANILINE		LIQU LIQU LIQU LIQU	1.7E-13 (5.7E-36) 3.3E-13 (7.8E-36)		1.9 1.9 1.3 1.3	R R NR NR		THG THG EFISH EFISH	MEREDITH MEREDITH LEVINE LEVINE	115 115 54 54	1983 1983 1976 1976
PYRIDINE		LIQU LIQU	9.9E-14 (3.4E-36)		1.9 1.9	R R		THG THG	MEREDITH MEREDITH	115 115	1983 1983
ACETONITRILE		LIQU LIQU	2.5E-14 (8.7E-37)		1.9 1.9	R R		THG THG	MEREDITH MEREDITH	115 115	1983 1983

CLASS: MISCELLANEOUS

MOLECULE/MATERIAL		NONLINEAR OPTICAL EFFECT					REFERENCES				
NAME	STRUCTURE	FORM	χ^3 or (γ) (esu)	n_2 (cm^2/MW)	λ (μm)	Res/NonRes	TIME	METHOD	AUTHOR	REF#	YEAR
METHANOL	<chem>CH3OH</chem>	LIQU	2.9E-14 (8.0E-37)		1.9	R		THG	MEREDITH	115	1983
		LIQU			1.9	R		THG	MEREDITH	115	1983
ETHANOL	<chem>CH3CH2OH</chem>	LIQU	3.7E-14 (1.3E-36)		1.9	R		THG	MEREDITH	115	1983
		LIQU			1.9	R		THG	MEREDITH	115	1983
2-PROPANOL	<chem>CH3CH(OH)CH3</chem>	LIQU	4.1E-14 (1.9E-36)		1.9	R		THG	MEREDITH	115	1983
		LIQU			1.9	R		THG	MEREDITH	115	1983
2-PROPANONE	<chem>CH3C(O)CH3</chem>	LIQU	4.4E-14 (2.0E-36)		1.9	R		THG	MEREDITH	115	1983
		LIQU			1.9	R		THG	MEREDITH	115	1983
TETRAHYDROFURAN	<chem>C1CCOC1</chem>	LIQU	5.0E-14 (2.2E-36)		1.9	R		THG	MEREDITH	115	1983
		LIQU			1.9	R		THG	MEREDITH	115	1983
METHYL CYCLOHEXANE	<chem>CC1CCCCC1</chem>	LIQU	5.9E-14 (4.6E-36)		1.9	R		THG	MEREDITH	115	1983
		LIQU			1.9	R		THG	MEREDITH	115	1983
CARBON TETRACHLORIDE	<chem>CCl4</chem>	LIQU	6.7E-14 (3.1E-36)		1.9	R		THG	MEREDITH	115	1983
		LIQU			1.9	R		THG	MEREDITH	115	1983
CHLOROFORM	<chem>CHCl3</chem>	LIQU	5.8E-14		1.9	R?		THG	MEREDITH	115	1983
TETRACHLOROETHANE	<chem>C2H2Cl4</chem>	LIQU	8.6E-14		1.9	R?		THG	MEREDITH	115	1983
O-NITROANILINE	<chem>Nc1ccc([N+](=O)[O-])cc1</chem>	LIQU	4.8E-12 (1.2E-34)		1.318	NR?		EFISH	LEVINE	54	1976
		LIQU			1.318	NR?		EFISH	LEVINE	54	1976

CLASS: MISCELLANEOUS

NAME	STRUCTURE	FORM	NONLINEAR OPTICAL EFFECT					REFERENCES			
			χ^3 or (γ) (esu)	n_2 (cm ² /MW)	λ (μ m)	Res/NonRes	TIME	METHOD	AUTHOR	REF#	YEAR
M-NITROANILINE		LIQU	3.3E-12		1.318	NR?		EFISH	LEVINE	54	1976
		LIQU	(8.5E-35)		1.318	NR?		EFISH	LEVINE	54	1976
P-NITROANILINE		LIQU	2.0E-11		1.318	NR?		EFISH	LEVINE	54	1976
		LIQU	(5E-34)		1.318	NR?		EFISH	LEVINE	54	1976
ALKANES	$\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_3$ n=6 n=8 n=10 n=16	LIQU	4.7E-14		1.064			THG	KAJZAR	52	1987
			5.0E-14		1.064			THG	KAJZAR	52	1987
			5.4E-14		1.064			THG	KAJZAR	52	1987
			6.0E-14		1.064			THG	KAJZAR	52	1987
	$\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_2\text{Cl}$ n=6 n=10 n=12 n=14	LIQU	5.6E-14		1.064			THG	KAJZAR	52	1987
			6.1E-14		1.064			THG	KAJZAR	52	1987
			6.5E-14		1.064			THG	KAJZAR	52	1987
			6.7E-14		1.064			THG	KAJZAR	52	1987
	$\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_2\text{Br}$ n=6 n=10 n=14	LIQU	7.5E-14		1.064			THG	KAJZAR	52	1987
			6.9E-14		1.064			THG	KAJZAR	52	1987
			6.9E-14		1.064			THG	KAJZAR	52	1987
	$\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_2\text{I}$ n=6 n=8 n=10	LIQU	1.3E-13		1.064			THG	KAJZAR	52	1987
			1.2E-13		1.064			THG	KAJZAR	52	1987
			1.0E-13		1.064			THG	KAJZAR	52	1987

MOLECULE/MATERIAL			NONLINEAR OPTICAL EFFECT					REFERENCES			
NAME	STRUCTURE	FORM	χ^3 or (γ) (esu)	n_2 (cm^2/MW)	λ (μm)	Res/NonRes	TIME	METHOD	AUTHOR	REF#	YEAR
<hr/>											
Pb/Sn FLUOROPHOSPHATE GLASS WITH ACRIDINE ORANGE (8E17 molecules/ cm^3) ACRIDINE YELLOW (8E17 molecules/ cm^3)			0.02 0.06	0.21 0.16	0.514 0.467	R R	msec msec	SATIN SATIN	TOMPKIN TOMPKIN	149 149	1987 1987
<hr/>											
BORIC ACID GLASS WITH FLUORESCIN (10E18 molecules/ cm^3)			1		0.467	R	sec	DFWM	KRAMER	148	1986
<hr/>											
$\text{CdS}_x\text{Se}_{1-x}$ DOPED GLASS			1E-8		0.588	R	ns	DFWM	ROSSIGNOL	30	1987
<hr/>											
CRYSTALS											
NaF				$7.7\text{E}-10^*$	1.060	NR			NASU	29	1987
NaCl				$1.8\text{E}-9^*$	1.060	NR			NASU	29	1987
NaBr				$7.8\text{E}-9^*$	1.060	NR			NASU	29	1987
KCl				$2.7\text{E}-9^*$	1.060	NR			NASU	29	1987
KBr				$1.1\text{E}-8^*$	1.060	NR			NASU	29	1987
CaF_2				$2.7\text{E}-9^*$	1.060	NR			NASU	29	1987
CdF_2				$1.2\text{E}-9^*$	1.060	NR			NASU	29	1987
CdS				$1.9\text{E}-7^*$	1.060	NR			NASU	29	1987
<hr/>											
GaAs			0.4 $1.2\text{E}-11$	$4\text{E}-4$ $1.1\text{E}-6^{**}$	0.820 1.3-13	NR			KOWEL CHANG	40 110	1987 1981
InSb			1 $8\text{E}-10$	$3\text{E}-3$ (77K) $6.5\text{E}-5^{**}$	5.4 9-24	NR			KOWEL CHANG	40 110	1987 1981
InAs			$1.8\text{E}-10$	$1.6\text{E}-5^{**}$	4-14	NR			CHANG	110	1981
Ge<111>			$1.5\text{E}-10$	$1\text{E}-5^{**}$	2-14	NR			CHANG	110	1981
Si<111>			$8.0\text{E}-12$	$7.1\text{E}-7^{**}$	1.3-7	NR			CHANG	110	1981
<hr/>											
HgTe		TF	$1.6\text{E}-4$ $-1\text{E}-4$		10.6 10.6		ns	non-DFWM	WOLFF HOFFMAN	181 191	1987 1988

HgTe/CdTe AND Hg₂Te/CdTe SUPERLATTICES
 * CONVERTED FROM esu TO cm^2/MW USING: $1 \text{ esu} = 8.1 \times 10^3 \text{ cm}^2/\text{MW}^{127}$
 ** CONVERTED FROM MKS (m^2/V^2) TO cm^2/MW USING: $1 \text{ MKS} = 7.3 \times 10^{12} \text{ cm}^2/\text{MW}^{127}$

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